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Cleavage of organosilicon compounds

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CLEAVAGE OF ORGANOSILICON COMPOUNDS.

Iowa State University of Science and Technology
Ph.D., 1962
Chemistry, organic

University Microfilms, Inc., Ann Arbor, Michigan

CLEAVAGE OF ORGANOSILICON COMPOUNDS

by

Richard Allen Tomasi

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

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1962

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INTRODUCTION

The relative ease of cleavage of the strained ring in octaphenylcyclotetrasilane lends a particular uniqueness to the study of the chemistry of silicon-silicon bonds. In general, reagents which will cleave this compound under mild conditions may also prove effective in cleaving silicon-silicon linkages in other organosilicon compounds under more forcing conditions. Conversely, substances which do not affect octaphenylcyclotetrasilane would not be expected to react with the disilane group in other compounds.

Thus, the research described in This Thesis is along those lines, with emphasis on reductive cleavages. Octaphenylcyclotetrasilane was treated with a variety of reducing agents. Of those tried, two systems were found which warranted further investigations. They are hydrogenolysis over "copper chromite" at relatively high temperatures and hydrogen pressures, and cleavage by lithium aluminum hydride in tetrahydrofuran. The latter reaction is interesting in that evidence supports the formation of intermediate organosilylaluminum compounds.

Some preliminary work was also carried out on the possibility of utilizing the Wittig reagent as a synthetic tool in organosilicon chemistry.

HISTORICAL

Within the voluminous literature concerned with the field of organosilicon chemistry, there appear only a few methods for the formation of silicon-hydrogen bonds. These techniques and other reactions which are reductive in nature will be presented herein, with emphasis on methods which involve cleavages of silicon-carbon and silicon-silicon bonds. A brief outline of the chemistry of octa-phenylcyclotetrasilane will also be included.

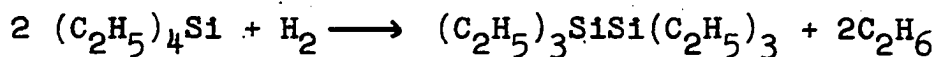
In addition to the usual sources of references, there has appeared three recent, excellent reviews which, because of their value as reference guides, warrant their mention here. One of these is a comprehensive book on the field of organosilicon chemistry covering the period of time prior to the middle of 1958.¹ The other two reviews deal with the subject of organosilylmetallic chemistry.²

¹C. Eaborn, "Organosilicon Compounds", Butterworths Scientific Publications, London, 1960.

²(a)D. Wittenberg and H. Gilman, *Quart. Rev.*, 13, 116 (1959); (b)H. Gilman and H. J. S. Winkler, "Organosilyl-metallic Chemistry", in H. Zeiss, ed., "Organometallic Chemistry", pp. 270-345, Reinhold Publishing Corporation, New York, N.Y., 1960.

Reactions Involving Hydrogen³

Initial attempts to cleave tetrasubstituted organo-silicon compounds by hydrogen at high temperatures and pressures gave only small amounts of silane (SiH_4), along with hydrocarbons and hexasubstituted disilanes. Thus, tetraethylsilane, when heated at 350° under hydrogen pressure, gave predominantly hexaethyldisilane and ethane,⁴ according to the following equation. Similarly, triethylphenylsilane



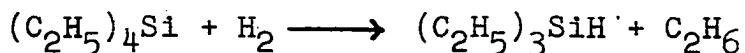
gave benzene, hexaethyldisilane, diethyldiphenylsilane, and tetraethylsilane.^{4,5} When tetraethylsilane was passed over an alumino-silicate catalyst at 550° in a stream of hydrogen, yields of triethylsilane as high as 54% were obtained.⁶

³For general surveys of organic reactions involving hydrogen, see H. Adkins, "Reactions of Hydrogen with Organic Compounds over Copper-chromium Oxide and Nickel Catalysts", University of Wisconsin Press, Madison, Wisc., 1937; H. Adkins and R. L. Shriner, "Catalytic Hydrogenation and Hydrogenolysis", in H. Gilman, ed., "Organic Chemistry, an Advanced Treatise", 2nd ed., Vol. 1, pp. 779-834, John Wiley and Sons, Inc., New York, N.Y., 1943.

⁴V. Ipatieff and B. N. Dolgov, Ber., 62B, 1220 (1929).

⁵B. N. Dolgov and Y. Volnov, Zhur. Obshchei Khim., 1, 91 (1931); [C. A., 25, 4535 (1931)].

⁶M. G. Voronkov, B. N. Dolgov, and G. B. Karpenko, Zhur. Obshchei Khim., 24, 269 (1954); [Original available but not translated; translated in J. Gen. Chem. U.S.S.R., 24, 271 (1954)].



Tetrabenzylsilane was found to be stable towards hydrogen at high pressures and temperatures around 400°. ⁵ This unreactivity of the silicon-benzyl group appears to be somewhat anomalous, since debenzylation occurs readily with oxygen, nitrogen, and sulfur derivatives. ⁷ However, the attempted reaction with tetrabenzylsilane was carried out in the absence of a catalyst. Tetraphenylsilane also did not react with hydrogen at temperatures up to 490° under high pressures without a catalyst. ⁴ Over Raney nickel, tetraphenylsilane and the series of methylphenyl-substituted monomers have been successfully hydrogenated to give the corresponding cyclohexyl derivatives in good yields. ⁸ These reactions were carried out at temperatures between 100-200° and pressures of 50-100 atmospheres. Unsuccessful attempts to effect similar hydrogenations of 1,1,2,2-tetraphenyldisilane and 1,2-dimethyl-1,1,2,2-tetraphenyldisilane are reported in This Thesis.

Halogenated silanes have been reduced by passing their vapors in a stream of hydrogen over silicon pellets at 310-350° in the presence of traces of aluminum chloride or bromide. ⁹ Compounds containing silicon-hydrogen bonds are

⁷W. H. Hartung and R. Simonoff, Org. Reactions, 7, 263 (1953).

⁸M. Kanazashi and M. Takakusa, Bull. Chem. Soc. Japan, 27, 269 (1954).

⁹O. B. Hatcher, U. S. Patent 2,458,703, Jan. 11, 1949; [C. A., 43, 3441 (1949)].

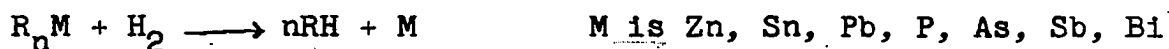
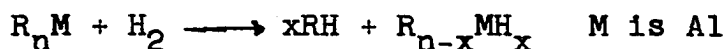
also formed as by-products in the direct synthesis of organo-silicon halides from elemental silicon (usually in the presence of metals such as copper) and organic halides at temperatures around 300-400°. ¹⁰ However, the yields are increased when the reactants are diluted with hydrogen. The vapor phase hydrogenation of chlorosilanes has also been shown to occur when mixtures of the halides and hydrogen are passed over metallic aluminum, magnesium, zinc or iron at temperatures of 300-500°. ¹¹ Silicon tetrachloride gave 3-5% of dichlorosilane and around 25% of silicochloroform. Similarly, silicochloroform gave 1-2% yields of silane and chlorosilane, in addition to 15% of dichlorosilane. However, trichloromethylsilane gave only about 5% of dichloromethylsilane, while attempts to reduce dichlorodimethylsilane were generally unsuccessful. ¹¹

The related hydrogenolysis reactions of organic derivatives of many metals and metalloids has been well established. These compounds react according to the following general equations. The conditions required to effect hydrogenolysis



¹⁰For a discussion of and leading references to the direct synthesis, see C. Eaborn, op. cit., pp. 36-44.

¹¹D. T. Hurd, J. Am. Chem. Soc., 67, 1545 (1945).



of these substances undergo a gradation which has been used to determine their relative reactivities.^{12,13,14} Thus, phenylsodium, -potassium, -rubidium, and -cesium react with hydrogen at room temperature and atmospheric pressure in the absence of added catalysts.¹² Organolithium reagents require pressures of a few atmospheres and longer reaction periods, while phenylcalcium iodide is incompletely reduced under these conditions.¹² Organic compounds of magnesium,^{13,15,16} aluminum,¹³ zinc,^{13,15} tin,^{13,15,17} and lead^{13,14,15} undergo hydrogenolysis at intermediate to relatively high temperatures and pressures, while derivatives of phosphorus, arsenic,

¹²H. Gilman, A. L. Jacoby, and H. Ludeman, ibid., 60, 2336 (1938).

¹³H. E. Podall, H. E. Petree, and J. R. Zietz, J. Org. Chem., 24, 1222 (1959).

¹⁴W. H. Zartman and H. Adkins, J. Am. Chem. Soc., 54, 3398 (1932).

¹⁵H. E. Podall and W. E. Foster, J. Org. Chem., 23, 1848 (1958).

¹⁶L. L. Garshbein and V. N. Ipatieff, J. Am. Chem. Soc., 74, 1540 (1952).

¹⁷V. N. Ipatieff, G. A. Razuvaev, and I. F. Bogdanov, Ber., 63B, 335 (1930).

antimony, and bismuth react only under extreme conditions.¹⁸

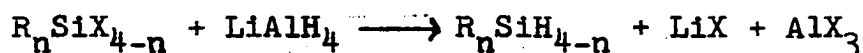
The attempted cleavage of hexaphenyldilead by hydrogen has been observed to give tetraphenyllead and elemental lead instead of triphenyllead hydride.¹³ The hydrogenolysis of phenyl-substituted disilane groups over "copper chromite" catalyst at relatively high temperatures and hydrogen pressures yielding organosilicon hydrides is reported in This Thesis. Hexaethyldisilane did not react under comparable conditions. The cleavage of silicon-silicon bonds has a close analogy in carbon chemistry in the hydrogenolysis of the aliphatic carbon-carbon bonds in phenyl-substituted ethanes.¹⁹ Thus, pentaphenyl-, 1,1,2,2-, and 1,1,1,2-tetraphenyl-, and even to a small extent 1,1,2-triphenylethane were cleaved by hydrogen over "copper chromite" to give the corresponding phenylated methanes.¹⁹ Aliphatic compounds were not affected under similar treatment.¹⁹ The use of a nickel catalyst provided the respective cyclohexylethanes, without appreciable cleavage of carbon-carbon bonds except in the reaction of pentaphenylethane,¹⁹ which may be due to dissociation into free radicals. The hydrogenolysis of silicon-silicon bonds reported herein was not appreciably catalyzed by Raney nickel.

¹⁸V. N. Ipatieff and G. A. Razuvaev, ibid., 1110 (1930).

¹⁹W. H. Zartman and H. Adkins, J. Am. Chem. Soc., 54, 1668 (1932).

Reduction with Metallic Hydrides²⁰

With the advent of lithium aluminum hydride in 1947,²¹ the synthesis of compounds containing silicon-hydrogen bonds was greatly simplified. It would not be practical in a man-



uscript of this size to give reference to the many compounds which have been prepared by use of this reagent. In general, reduction of most organosilicon halides proceeds smoothly in diethyl ether with little trouble from side reactions. Other higher boiling ethers, such as tetrahydrofuran, dioxane, or ethylene glycol dimethyl ether have also been used in cases where more vigorous conditions are required, such as with the preparation of tris(2-biphenyl)silane.²² Hydrides have also been obtained from organosilicon alkoxides²³ at 100° in the absence of solvent or in di-n-butyl ether, and from siloxanes in ether.^{24,25} It has been reported that

²⁰For a review on the chemistry of metallic hydrides, see N. G. Gaylord, "Reduction with Complex Metal Hydrides", Interscience Publishers, Ltd., New York, N.Y., 1956.

²¹A. E. Finholt, A. G. Bond, Jr., K. E. Wilzbach, and H. I. Schlesinger, J. Am. Chem. Soc., **69**, 2692 (1947).

²²H. Gilman and K. Oita, J. Org. Chem., **20**, 862 (1950).

²³H. Westmark, Acta Chem. Scand., **8**, 1830 (1954).

²⁴N. C. Harvey, W. H. Nebergall, and J. S. Peak, J. Am. Chem. Soc., **79**, 1437 (1957).

²⁵G. Fritz, Z. Naturforsch., **10b**, 423 (1955).

even quartz sand slowly evolves silane when treated with lithium aluminum hydride.²⁵ The preparation of disilane (Si_2H_6) from the hexachloride in ether was found to proceed satisfactorily when a solution of lithium aluminum hydride was added to the chloro compound.²¹ However, reverse addition gave exclusively silane (SiH_4) when the reduction was carried out in tetrahydrofuran or di-n-butyl ether.²⁶ It has recently been demonstrated that disilane is cleaved by potassium hydride in ethylene glycol dimethyl ether to yield silane and silylpotassium, as illustrated in the following equation.²⁷



A similar reaction has been observed in the reduction of 1,1,2,2-tetrabutyltin 1,2-dichloride by lithium aluminum hydride, which resulted in the formation of di-n-butyltin dihydride.²⁸ These cleavages are analogous to reactions reported in This Thesis, wherein silicon-silicon bond fission results from the treatment of phenyl-substituted di- and polysilanes with lithium aluminum hydride in tetrahydrofuran.

²⁶H. S. Gutowsky and E. O. Stejskal, J. Chem. Phys., 22, 939 (1954).

²⁷M. A. Ring and D. M. Ritter, J. Am. Chem. Soc., 83, 802 (1961).

²⁸J. G. Noltes, unpublished Ph. D. Thesis, University of Utrecht, Holland, 1958; [Original not available; cited in R. K. Ingham, S. D. Rosenberg, and H. Gilman, Chem. Rev., 60, 507 (1960)].

A previous attempt to cleave hexaphenyldisilane in ether by lithium aluminum hydride was unsuccessful.²⁹

It has been shown that partial reduction of compounds containing more than one silicon-halogen group is not possible.³⁰ For example, phenylsilane was the only reduction product obtained from the treatment of excess trichlorophenylsilane with lithium aluminum hydride.

Although "flank" attack on silicon by hydride has been demonstrated in the reaction of chlorides containing silicon at the bridgehead of bicyclic systems,³¹ recent evidence has shown that the reduction of an optically active chlorosilane occurs primarily with inversion.³²

Lithium hydride has also been used to reduce chlorosilanes, but higher temperatures are needed, such as at the boiling points of dioxane or di-n-butyl ether.²¹ Sodium hydride does not react at the boiling point of dioxane,

²⁹T. C. Wu and H. Gilman, J. Org. Chem., 23, 913 (1958).

³⁰J. L. Speier, R. Zimmerman, and J. Webster, J. Am. Chem. Soc., 78, 2278 (1956); M. C. Harvey, W. H. Nebergall, and J. S. Peake, ibid., 76, 4555 (1954); and H. E. Opitz, J. S. Peake, and W. H. Nebergall, ibid., 78, 292 (1956).

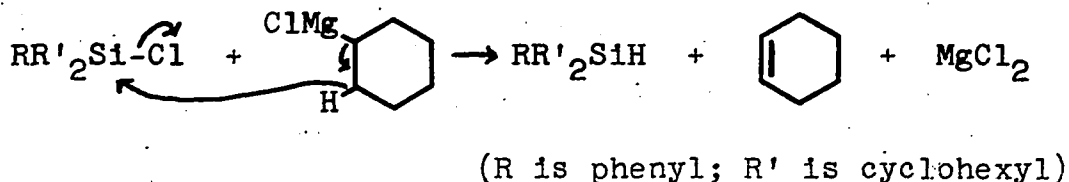
³¹L. H. Sommer, O. F. Bennett, P. G. Campbell, and D. R. Weyenberg, ibid., 79, 3295 (1957); L. H. Sommer and O. F. Bennett, ibid., 81, 251 (1959).

³²L. H. Sommer and C. L. Frye, ibid., 81, 1013 (1959); L. H. Sommer and C. L. Frye, ibid., 82, 4118 (1960); L. H. Sommer, C. L. Frye, M. C. Musolf, G. A. Parker, P. G. Rodewald, K. W. Michael, Y. Okaya, and R. Pepinsky, ibid., 83, 2212 (1961).

unless a catalytic amount of aluminum chloride is present.²¹ In general, there is usually no advantage in the use of these reagents over lithium aluminum hydride.

Chlorotrimethylsilane has been found to be inert towards sodium or potassium borohydrides even at 130°.³³ It reacted rapidly with aluminum borohydride, but disproportionation also occurred, yielding tetramethylsilane and dimethylsilane in addition to the expected trimethylsilane.³³

Related hydride reductions of organosilicon halides and alkoxides have been observed in reactions where steric factors are involved.³⁴ For example, the reaction of trichlorophenylsilane with excess cyclohexylmagnesium chloride proceeds through two stages giving chlorodicyclohexylphenylsilane. However, further reaction gives dicyclohexylphenylsilane and cyclohexene instead of the expected tricyclohexylphenylsilane,^{34b} as shown in the following equation.



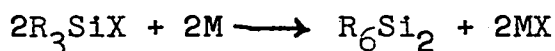
³³N. C. Goodspeed and R. T. Sanderson, J. Inorg. Nucl. Chem., 2, 267 (1956).

³⁴(a)N. W. Cuss and F. S. Kipping, J. Chem. Soc., 1933, 1040; (b)W. H. Nebergall and J. S. Peake, J. Am. Chem. Soc., 79, 2762 (1957).

Reactions with Metals

Organosilicon halides

In general, the reactions of organosilicon halides with alkali metals is the conventional method used to prepare compounds containing disilane bonds. The reported "direct synthesis" of triphenylsilyllithium and other silylmetallic



compounds from the halides and metals³⁵ has been shown to proceed, at least in part if not exclusively, by initial coupling and subsequent cleavage of the resulting disilane.³⁵ Thus, to date there has been no established instance of the preparation of silylmetallic compounds directly from a halide and metal, a reaction which is common in carbon chemistry. This type of compound is most likely present as intermediates in the coupling reactions.

Recently, it has been shown that organosilicon compounds may be coupled with magnesium.^{35,36} Here, the elusive silyl-Grignard reagent may well be intermediately involved. Magnesium was found to react with bromosilane and iodosilane, but the formation of silylmagnesium compounds was not estab-

³⁵H. Gilman, D. J. Peterson, and D. Wittenberg, Chem. Ind., 1958, 1479; M. V. George, D. J. Peterson, and H. Gilman, J. Am. Chem. Soc., **82**, 403 (1960).

³⁶(a)W. Steudel and H. Gilman, J. Am. Chem. Soc., **82**, 6129 (1960); (b)H. J. S. Winkler and H. Gilman, J. Org. Chem., **26**, 1265 (1961).

lished.^{37,38} Evidence of a transient triphenylsilylmagnesium halide was obtained from the reaction of cyclohexylmagnesium bromide with chlorotriphenylsilane in tetrahydrofuran by the formation of hexaphenyldisilane, the normal coupling product.³⁹ The isolation 1,1,1-trimethyl-2,2,2-triphenyldisilane when the reaction was carried out in the presence of chlorotrimethylsilane further supports an intermediate silyl-Grignard reagent.³⁹

Dichlorodimethylsilane, when heated at high temperatures with aluminum metal, yielded some aluminum chloride.¹¹ There was no evidence of the formation of disilanes; however, a darkening of the aluminum occurred, which was considered to be due to the deposition of elemental silicon.

Iodosilane was found to react with zinc and mercury yielding hydrogen, silane, and disilane,³⁷ but the formation of silylmetallic compounds was not confirmed.⁴⁰

Cleavage of silicon-silicon bonds

The cleavage of silicon-silicon bonds by alkali metals is the standard method for the preparation of organosilylmetallic compounds, a subject which has been the topic of

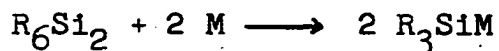
³⁷H. J. Emeléus, A. G. Maddox, and C. Reid, J. Chem. Soc., 1941, 353.

³⁸E. R. Van Artsdalen and J. Gavis, J. Am. Chem. Soc., 74, 3196 (1952).

³⁹T. G. Selin and R. West, Tetrahedron, 5, 97 (1959).

⁴⁰A. G. MacDiarmid, Quart. Rev., 10, 208 (1956).

two recent reviews.² In general, the reactions take the course illustrated in the following equation. Organodisilanes



have been cleaved by alkali metals under a variety of conditions. Cleavage by lithium in tetrahydrofuran is the method of choice for the preparation of organosilylmetallic compounds.⁴¹ Organosilyllithium reagents prepared in tetrahydrofuran are obtained in high yields and form homogeneous solutions which are easy to handle and have appreciable stability. These advantages are not all realized in other systems. Lithium cleavage of hexaphenyldisilane has been observed in ethylene glycol dimethyl ether,⁴² tetrahydropyran, dioxane,^{43,44} and pyridine.⁴⁵ Hexaphenyldisilane has also been cleaved by the following metal and solvent systems: sodium/potassium alloy in diethyl ether,^{46,47}

⁴¹H. Gilman and G. D. Lichtenwalter, J. Am. Chem. Soc., **80**, 608 (1958).

⁴²A. G. Brook and H. Gilman, ibid., **76**, 278 (1956).

⁴³M. V. George and H. Gilman, ibid., **81**, 3288 (1959).

⁴⁴D. Wittenberg, D. Aoki, and H. Gilman, ibid., **80**, 5933 (1959).

⁴⁵D. Wittenberg and H. Gilman, Chem. Ind., **1958**, 390.

⁴⁶H. Gilman and T. C. Wu, J. Org. Chem., **18**, 753 (1953).

⁴⁷H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman, and S. H. Eidt, J. Am. Chem. Soc., **74**, 561 (1958).

ethylene glycol dimethyl ether,⁴² and to a small extent in solvents such as petroleum ether and benzene;⁴⁶ sodium in liquid ammonia;^{29,47} potassium in di-n-butyl ether;⁴⁶ and rubidium and cesium in diethyl and di-n-butyl ethers.⁴⁶

No cleavage of hexaphenyldisilane was observed by: sodium dispersion in ether, tetralin,⁴⁸ xylene, or dioxane;⁴⁹ calcium or magnesium in tetrahydrofuran;⁵⁰ or magnesium in diethyl or di-n-butyl ethers.^{41,45} Unsuccessful attempts to cleave silicon-silicon bonds by a mixture of magnesium and magnesium halide or by aluminum in tetrahydrofuran are reported in This Thesis.

The preparation of methyldiphenylsilyllithium and dimethylphenylsilyllithium by cleavage of the corresponding disilanes has been accomplished in tetrahydrofuran,⁴¹ but similar cleavages by sodium/potassium alloy in ether did not proceed satisfactorily.^{51,52}

⁴⁸T. C. Wu, "Comparisons of Some Organic Compounds Containing Group IV-B Elements", unpublished Ph. D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa, 1952.

⁴⁹H. Gilman and T. C. Wu, J. Am. Chem. Soc., **73**, 4031 (1951).

⁵⁰G. D. Lichtenwalter, "Organosilylmetallic Compounds and Derivatives", unpublished Ph. D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa, 1958.

⁵¹H. Gilman, R. K. Ingham, and A. G. Smith, J. Org. Chem., **18**, 1743 (1953).

⁵²A. G. Smith, "Some Cleavage Reactions of Alkyl and Aryl Silanes", unpublished M. S. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa, 1953.

In sharp contrast to the reactions of phenyl-substituted compounds, there has been no similar cleavages of hexaalkyldisilanes. Hexamethyldisilane^{51,53} and hexaethyldisilane⁴⁸ were not cleaved in ethers by sodium/potassium alloy. Similarly, hexaethyldisilane did not react with: lithium in tetrahydrofuran,^{50,54} ethylene glycol dimethyl ether, ethylamine,⁵⁵ or trimethylamine;⁵⁰ sodium/potassium alloy at elevated temperatures in the absence of solvents,^{51,52} in ether containing a little tetrahydrofuran, or in ethylene glycol dimethyl ether;⁵¹ sodium in liquid ammonia;^{51,52} rubidium without solvent;⁵¹ or by cesium in a mixture of diethyl and di-n-butyl ethers.⁵² Low yields of trialkylsilylmetallic compounds have been obtained by fission of 1,1,1-trialkyl-2,2,2-triphenyldisilanes. Thus, as determined by derivatization with bromobenzene, low yields of trimethylsilylpotassium were obtained with sodium/potassium alloy in ether.⁵¹ Similarly, triethylsilyllithium was obtained in low yield by the lithium cleavage of 1,1,1-triethyl-2,2,2-triphenyldisilane in tetrahydrofuran.^{2a}

⁵³M. P. Brown and G. W. A. Fowles, J. Chem. Soc., 1958, 2811.

⁵⁴M. B. Hughes, "Some Correlations between Organosilicon and Organogermanium Compounds", unpublished Ph. D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa, 1958.

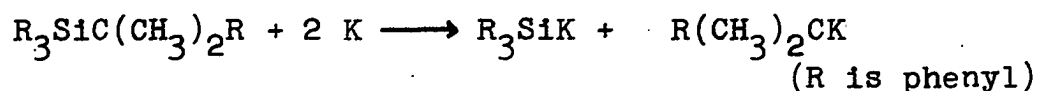
⁵⁵C. A. Kraus and W. K. Nelson, J. Am. Chem. Soc., 56, 195 (1934).

Analogous cleavages of silicon-germanium bonds by metals have also been observed, reactions which lead to a mixture of silyl- and germymetallic compounds. Thus, triethylsilyltriphenylgermane yielded triethylsilane and triphenylgermane when reacted with lithium in ethylamine.⁵⁵ A similar cleavage of triphenylsilyltriphenylgermane by sodium/potassium alloy in ether has been observed.⁵⁶ The cleavage of the silicon-tin bond in triphenylsilyltrimethyltin by sodium in liquid ammonia has also been reported.⁵⁷

The cleavage of silicon-silicon bonds by lithium aluminum hydride in tetrahydrofuran reported in This Thesis occurs with phenyl-substituted compounds, while hexaethyldisilane was unaffected.

Cleavage of silicon-carbon bonds

One of the earliest preparations of triphenylsilyl-potassium was by the cleavage of (α,α -dimethylbenzyl)triphenylsilane by sodium/potassium alloy in diethyl ether.⁵⁸

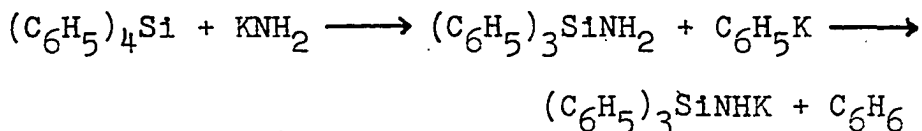


⁵⁶H. Gilman and C. W. Gerow, *ibid.*, 78, 5823 (1956).

⁵⁷C. A. Kraus and H. Eatough, *ibid.*, 55, 5008 (1933).

⁵⁸R. A. Benkeser and R. G. Severson, *ibid.*, 73, 1424 (1951).

α,α -Dimethylbenzylpotassium was also obtained. At about the same time, potassium in liquid ammonia was observed to cleave silicon-benzyl groups in benzyltrimethylsilane, diphenylmethyltrimethylsilane, and triphenylmethyltrimethylsilane.⁵⁹ Shortly thereafter, this reaction was extended to tetraphenylsilane,⁶⁰ as illustrated in the following equation. The



formation of the silicon-nitrogen bond could also have arisen by the reaction of triphenylsilylpotassium with solvent. Similar cleavages have also been observed by lithium in ethylamine.⁶¹

Silicon-phenyl groups have also been cleaved by sodium/potassium alloy in ether in the "apparent redistribution" reactions of phenyl- and diphenylsilane,^{62,63} as illustrated

⁵⁹C. R. Hauser and C. R. Hance, ibid., 5846 (1951).

⁶⁰Ibid., 74, 1856 (1952).

⁶¹R. A. Benkeser, R. E. Robinson, and H. Landesman, ibid., 5699 (1952).

⁶²R. A. Benkeser, H. Landesman, and D. J. Foster, ibid., 648 (1952).

⁶³R. A. Benkeser and D. J. Foster, ibid., 4200 (1952).

in the following equations. Hydrolysis of the intermediate



(R is C_6H_5 ; R' is R or H)

silylmetallic compounds led to the formation of the corresponding silicon hydrides. Similar reactions have been observed at elevated temperatures in decalin.⁶⁴ From the reactions of methyldiphenylsilane and dimethylphenylsilane, products were obtained which indicated that cleavage of phenyl groups occurred in preference to methyl groups.⁶⁴ Similar cleavages of phenyl-silicon bonds have been observed by lithium in ether and tetrahydrofuran.⁶⁵ The reaction of benzyltriphenylsilane with lithium in tetrahydrofuran was found to cleave both phenyl and benzyl groups.⁶⁶ Benzyl groups have also been observed to undergo cleavage from silicon by alkali metals in hydrocarbon solvents.^{64,67}

Many unsuccessful attempts to cleave silicon-carbon

⁶⁴Ibid., 5314 (1952).

⁶⁵R. D. Gorsich, "Some Cyclic Organosilicon Compounds and Derivatives", unpublished Ph. D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa, 1957.

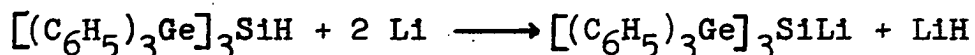
⁶⁶H. Gilman, H. A. McNinch, and D. Wittenberg, J. Org. Chem., **23**, 2044 (1958).

⁶⁷A. R. Steele and F. S. Kipping, J. Chem. Soc., **1928**, 1431.

bonds have been carried out for the preparation of trialkylsilylmetallics. For example, the following compounds were not cleaved under the conditions indicated: trimethylphenylsilane,⁵¹ triethylphenylsilane,^{51,54} 2-biphenyltrimethylsilane,⁵⁴ and trimethyl-o-tolylsilane,⁵⁴ by sodium/potassium alloy in ether; triethylphenylsilane by sodium in liquid ammonia or lithium in ethylamine;⁵⁵ trimethylphenylsilane, triethylphenylsilane, 9-fluorenyltrimethylsilane, and 9,9-bis(trimethylsilyl)fluorene by lithium in ether or tetrahydrofuran.⁵⁴

Cleavage of silicon-hydrogen bonds

The first established example of a silyllithium compound of appreciable stability was obtained by the treatment of tris(triphenylgermyl)silane with lithium in ethylamine.⁶⁸ The reaction is illustrated in the following equation. This



silyllithium compound could be derivatized with ethyl bromide, but it did react slowly with the solvent to form a silicon-nitrogen containing product.⁶⁸ Similar silyl amines have been obtained from the reaction of triethylsilane and lithium in

⁶⁸J. G. Milligan and C. A. Kraus, J. Am. Chem. Soc., **72**, 5297 (1950).

ethylamine⁵⁵ and from triphenylsilane and sodium in liquid ammonia.⁶⁹ Although they may have arisen through reaction of intermediate silylmetallic compounds with solvent, another route was considered more likely, as illustrated in the following reaction sequence.



(R is ethyl or phenyl; R' is H or ethyl)

Although the "apparent redistribution" reactions of phenyl- and diphenylsilane led to the cleavage of both phenyl and hydrogen groups, the reaction with triphenylsilane with sodium/potassium alloy in ether gave primarily triphenylsilylpotassium.^{62,63} A similar reaction has been observed with lithium in tetrahydrofuran⁶⁵ and by sodium/potassium alloy at elevated temperatures in hydrocarbon solvents.⁶⁴ No reaction was observed between sodium/potassium alloy and triethylsilane in ether.⁶²

Cleavage of silicon-oxygen bonds

Alkoxytriarylsilanes have been cleaved by sodium/potassium alloy in ether to give the corresponding silylmetallic compound and the alkoxide,⁶² but no appreciable reaction occurred with sodium in xylene.⁴⁵ No reaction was observed with ethoxytrimethylsilane when treated with lithium⁵⁴ or

⁶⁹H. H. Reynolds, L. A. Bigelow, and C. A. Kraus, ibid., 51, 3067 (1929).

sodium/potassium alloy^{48,54} in ether or tetrahydrofuran, or with cesium in ether.⁵² This is in keeping with the difficulty of preparing trialkylsilylmetallic compounds. It has recently been found that certain siloxanes are cleaved by lithium, cesium, and rubidium in tetrahydrofuran to give the corresponding silylmetallic reagent and metal silanolate.⁷⁰ Hexamethyldisiloxane did not react under comparable conditions. The reaction of silicon-oxygen bonds with metals is shown in the following equation.



(R is aryl groups; R' is alkyl, triarylsilyl or trialkylsilyl groups)

Attempted indirect preparations of triphenylsilylmetallic compounds

Attempts^{50, 71-73} to obtain organosilylmetallic compounds by the reaction of triphenylsilyllithium with various

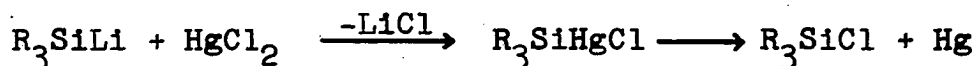
⁷⁰M. V. George and H. Gilman, Chemistry Department, Iowa State University of Science and Technology, Ames Iowa. Results from cleavage studies, private communication, 1961.

⁷¹M. V. George, G. D. Lichtenwalter, and H. Gilman, J. Am. Chem. Soc., 81, 978 (1959).

⁷²M. V. George, B. J. Gaj, and H. Gilman, J. Org. Chem., 24, 624 (1959).

⁷³B. J. Gaj, "Reactions of Triphenylsilyllithium with Compounds Containing Group VB Elements", unpublished Ph. D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa, 1960.

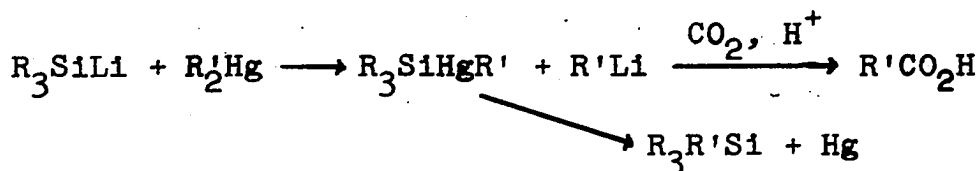
metallic compounds were generally without success. Reactions with halides of mercury (I), mercury (II), lead (II), tin (II), tin (IV), silver, copper (II), and iron (III) yielded appreciable amounts of hexaphenyldisilane, chlorotriphenylsilane, and triphenylsilane when worked up under anhydrous conditions.⁷¹ The reactions with mercury compounds also provided free mercury. The proposed course of the reaction is illustrated in the following equation.⁷¹ Some of the chlorotri-



phenylsilane thus formed could react with triphenylsilyllithium to give hexaphenyldisilane. Apparently, analogous reactions occurred with the other "intermediate" organosilylmetallic compounds.⁷¹ Similar results were obtained from the reaction of triphenylsilyllithium with phosphorus trihalides, phosphorus oxychloride, arsenic, antimony, and bismuth trichlorides.⁷² The formation of triphenylsilane prior to hydrolysis is not completely understood, but may be the result of decomposition into free radicals which could abstract hydrogen from solvent. A free-radical mechanism has been suggested to explain the isolation of triphenylsilane from the reaction of triphenylsilyllithium with molecular oxygen.⁴³ Triphenylsilane could also result from metalation of tetrahydrofuran. However, none of this product was reported from the reaction of triphenylsilyllithium with tetra-

hydrofuran at elevated temperatures, the primary product being 4-hydroxybutyltriphenylsilane resulting from cleavage of the solvent.^{65,74}

The reaction with phenylmercuric halides also gave some hexaphenyldisilane, but the major product was tetraphenylsilane.⁷¹ Tetraphenylsilane was also isolated from treatment of diphenylmercury with triphenylsilyllithium. Carbonation of the reaction mixture gave benzoic acid in good yields. When the reaction was carried out on di-p-tolylmercury, p-toluic acid and triphenyl-p-tolylsilane were obtained subsequent to carbonation. A mechanism accounting for these results is shown in the following equation.⁷¹ Similar results were also obtained with triphenylarsine, triphenyl-



(R is phenyl; R' is R or p-tolyl)

stibine, and triphenylbismuthine.⁷³

The solution obtained from the treatment of magnesium bromide with triphenylsilyllithium in tetrahydrofuran contained an organometallic compound, as indicated by a positive Color Test I.⁷⁵ Also, addition of chlorotriphenylsilane

⁷⁴D. Wittenberg and H. Gilman, J. Am. Chem. Soc., 80, 2677 (1958).

⁷⁵H. Gilman and F. Schulze, ibid., 47, 2002 (1925).

yielded hexaphenyldisilane in good yield. However, this reaction was not investigated further to determine if triphenylsilylmagnesium bromide was actually present.⁵⁰ Triphenylsilyllithium was also allowed to react with aluminum chloride and zinc chloride in one to one mole ratios.⁷¹ Other than the fact that hexaphenyldisilane was not formed, these reactions were not investigated further to establish if silylmetallic compounds resulted.⁷¹ The reaction between triphenylsilyllithium and aluminum chloride (in a three to one mole ratio, respectively) is reported in This Thesis. Hydrolysis of a part of the resulting mixture in deuteriochloric acid afforded some triphenylsilane which contained only small amounts of deuterated product, indicating that under these conditions, silylaluminum compounds are not formed in appreciable amounts. However, as reported herein, organosilylaluminum compounds are evidently obtained from the cleavage of silicon-silicon bonds by lithium aluminum hydride in tetrahydrofuran.

The reaction between triphenylsilyllithium and cadmium chloride was carried out at -60° , yielding a suspension which gave a negative Color Test I⁷⁵ for silyllithium.^{50,71,76} Upon warming to room temperature, metallic cadmium resulted. Attempts to isolate a silylcadmium compound were unsuccess-

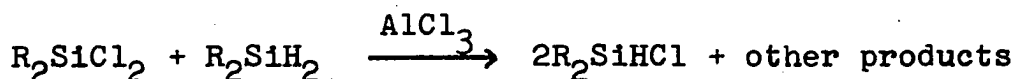
⁷⁶H. Gilman and W. H. Atwell, Chemistry Department, Iowa State University of Science and Technology, Ames, Iowa. Results from studies in the field of organosilicon chemistry, private communication, 1961.

ful.⁵⁰ However, treatment of the cold mixture with acid chlorides produced carbinols instead of the ketones,⁷⁶ as would have been expected if a silylcadmium reagent has a reactivity similar to other organocadmium compounds.⁷⁷

Other Methods of Forming Silicon-hydrogen Bonds

Disproportionation reactions

The formation of new silicon-hydrogen bonds has been demonstrated in redistribution reactions.⁷⁸ The reactions



are usually catalyzed by aluminum halides; however, thermal disproportionation of diphenylsilane has been reported.⁷⁹ Silicon-halogen, -alkoxide, and -carbon groups may be interchanged by this means. The use of triethylsilane as a source of hydrogen for the reduction of a number of organosilicon halides in high yields has been demonstrated.⁸⁰

⁷⁷For a survey on the preparation of ketones by the use of organometallic reagents, see D. A. Shirley, Org. Reactions, 8, 28 (1954).

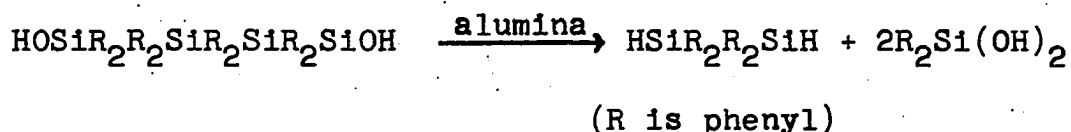
⁷⁸For a discussion of and leading references to redistribution reactions, see C. Eaborn, op. cit., pp. 197-198.

⁷⁹H. Gilman and D. H. Miles, J. Org. Chem., 23, 326 (1958).

⁸⁰S. N. Borisov, M. G. Voronkov, and B. N. Dolgov, Doklady Akad. Nauk S.S.S.R., 114, 93 (1957); [Original available but not translated; translated in Proc. Acad. Sci. U.S.S.R., 114, 433 (1957)].

Cleavage of silicon-silicon bonds

Investigations on the hydrolysis of 1,4-dichloroocta-phenyltetrasilane showed that 1,1,2,2-tetraphenyldisilane was obtained in yields as high as 20%.⁸¹ This product was obtained subsequent to chromatography on an alumina column. It was proposed that the cleavage was accomplished by acid catalyzed hydrolysis of the silicon-silicon bond present in the tetraphenyldisilan-ol group.^{81b} It has since been shown that similar cleavages of phenyl-substituted polysilan-ols occur when the substances are chromatographed on alumina in the absence of added acids.⁸² The following equation is illustrative.

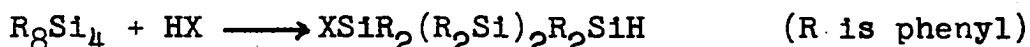


The chemistry of octaphenylcyclotetrasilane is described in the next section of This Historical. However, it should be noted here that this compound has been cleaved by anhydrous hydrogen chloride, bromide, and iodide to form 1-halo-

⁸¹(a)H. Gilman and W. Steudel, Chem. Ind., 1959, 1094;
(b)A. W. P. Jarvie and H. Gilman, ibid., 1960, 1271.

⁸²G. Chainani and H. Gilman, Chemistry Department, Iowa State University of Science and Technology, Ames, Iowa. Results from studies on organopolysilanes, private communication, 1961.

1,1,2,2,3,3,4,4-octaphenyltetrasilane.⁸³ This method for the formation of silicon-hydrogen bonds is unique.



The Chemistry of Octaphenylcyclotetrasilane

In a series of papers, Kipping and co-workers⁸⁴ described the reaction of dichlorodiphenylsilane with sodium. A complex mixture of products was obtained, from which they isolated two high-melting, well characterized, crystalline materials. One of these was quite insoluble in common organic solvents and melted "around 335°". This compound was designated as Compound (A) or "unsaturated". The other material did not melt at 360° and was soluble in benzene and toluene; this product was referred to as Compound (B), or "saturated". On the basis of molecular weight determinations and other analytical data, it was concluded that both of these materials had the molecular formula $(C_6H_5)_8Si_4$. Therefore, the structures of these compounds were based on chemical transformations. Compound (A) was found to undergo

⁸³H. Gilman, G. L. Schwebke and D. R. Chapman, Chemistry Department, Iowa State University of Science and Technology, Ames, Iowa. Results from studies on polysilanes, private communication, 1961.

⁸⁴F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, 119, 830, 848 (1921); F. S. Kipping, *ibid.*, 123, 2590, 2598 (1923); F. S. Kipping, *ibid.*, 125, 2291 (1924); F. S. Kipping, *ibid.*, 1927, 2719, 2728; F. S. Kipping and A. G. Murray, *ibid.*, 1929, 360; A. R. Steele and F. S. Kipping, *ibid.*, 1929, 2545; and F. S. Kipping, *Proc. Roy. Soc.*, 159A, 139 (1937).

the following reactions: it yellowed on standing in air and underwent a more rapid atmospheric oxidation when refluxed with toluene; it was oxidatively decomposed by boiling in nitrobenzene, aniline, benzyl alcohol, phenol, acetophenone, paraldehyde, and amyl nitrite; upon heating, halogen was readily abstracted from tetrachloroethane, dibromoethane, and phosphorus tribromide, with a dihalide being formed, $(C_6H_5)_8Si_4X_2$; and it reacted readily at room temperature with iodine to give the corresponding diiodide. In sharp contrast, Compound (B) was found to be relatively unreactive. It was therefore concluded that Compound (A) consisted of a linear chain of four diphenylsilylene units with tervalent silicons at the terminal positions. Apparently due to steric hindrance, the proposed diradical was not readily cyclized to a four-membered ring, the structure they assigned to the "isomeric" Compound (B).⁸⁴

A reinvestigation of these compounds was undertaken in This Laboratory when it was found that they were formed by the reaction of dichlorodiphenylsilane and lithium in tetrahydrofuran.⁸⁵⁻⁸⁸ By means of paramagnetic resonance studies,

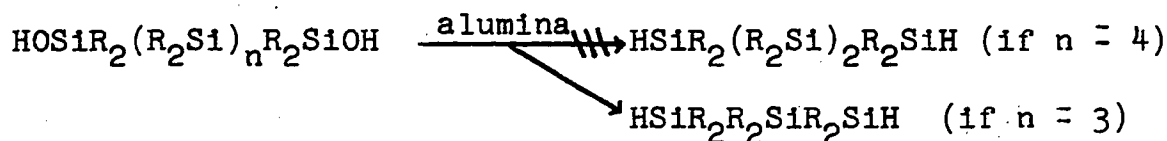
⁸⁵A. W. P. Jarvie, H. J. S. Winkler, D. J. Peterson, and H. Gilman, J. Am. Chem. Soc., 83, 1921 (1961).

⁸⁶Ibid., 82, 2076 (1960).

⁸⁷Ibid., 83, 4089 (1961).

⁸⁸H. Gilman, D. J. Peterson, A. W. Jarvie, and H. J. S. Winkler, Tetrahedron Letters, No. 23, 5 (1960).

a method not available to Kipping and co-workers, it was shown that Compound (A) did not contain tervalent silicon.⁸⁶ Furthermore, the structure of Compound (A) was shown to be the four-membered ring, octaphenylcyclotetrasilane.^{85,86} The structure of Compound (B), which Kipping, et al.⁸⁴ thought was the four-membered ring, has recently been proposed to be dodecaphenylcyclohexasilane.^{87,88} The evidence is based primarily on molecular weight determinations, but also on some derivatives.^{87,88} However, NMR data indicate that many derivatives from Compound (B) are pentasilanes instead of hexasilanes.^{82,89,90} Also, the dihydroxide, obtained by hydrolysis of the dibromide resulting from the reaction of Compound (B) with bromine, yielded 1,1,2,2,3,3-hexaphenyltrisilane when eluted from an alumina column, instead of the expected tetrasilane.⁸²



These recent observations^{82,89,90} are very indicative that Compound (B) is decaphenylcyclopentasilane instead of the six-membered cyclic homolog. This cyclic compound will

⁸⁹H. Gilman and K. Y. Chang, Chemistry Department, Iowa State University of Science and Technology, Ames, Iowa. Results from studies on polysilanes, private communication, 1961.

⁹⁰H. Gilman and G. L. Schwebke, ibid.

be referred to herein as Compound (B).

It should be stated here that the reactions of octaphenylcyclotetrasilane, Compound (A), which were reported by Kipping and co-workers,⁸⁴ have been confirmed in This Laboratory. In addition to these reactions and the cleavages by lithium aluminum hydride and by hydrogen reported in This Thesis, the following transformations have been observed.

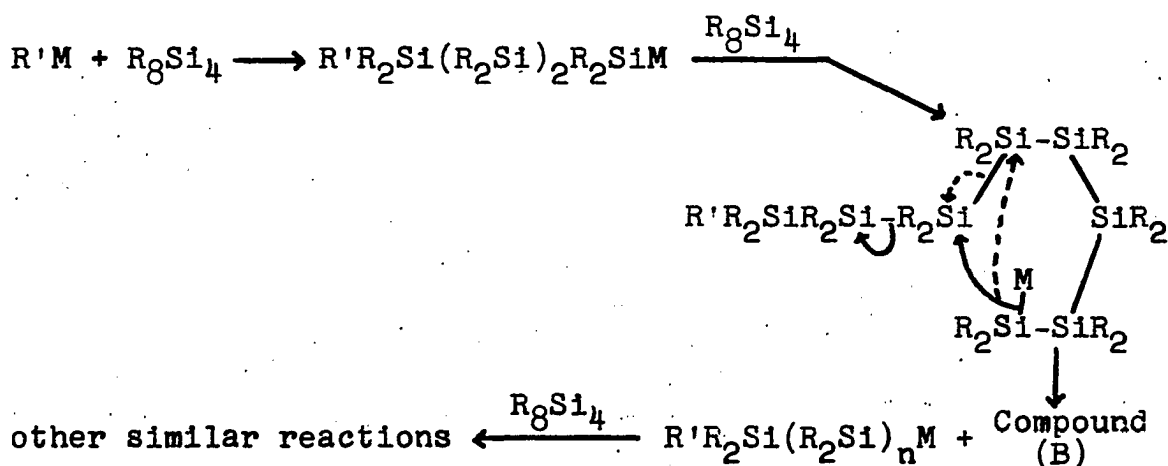
The abstraction of halogen from tetrachloroethane and dibromoethane observed by Kipping has been extended to a large number of organic halides:⁹¹ for example, bromoform, chloroform (under u. v. irradiation), dichlorodiphenylmethane, and 1,2-dichloro-1,1,2,2-tetraphenylethane. Tetraphenylethylene was also isolated from the reaction of the latter two compounds. High yields of 1,4-dichloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane have also been obtained from reactions with mercuric chloride,⁹² stannic chloride,⁹² thionyl chloride,⁷⁶ sulfuryl chloride⁷⁶ and phosphorus pentachloride.⁷⁶

As mentioned previously, octaphenylcyclotetrasilane has been cleaved by hydrogen bromide and hydrogen iodide in refluxing benzene and with hydrogen chloride in boiling o-dichlorobenzene.⁸³

⁹¹J. M. Kraemer and H. Gilman, J. Org. Chem., submitted for publication in 1961.

⁹²H. Gilman and A. W. P. Jarvie, Chem. Ind., 1960, 965.

The reaction of octaphenylcyclotetrasilane with organo-metallic compounds can lead to a variety of products.^{89,90,93} Under mild conditions and long reaction times, one of the main products is Compound (B). This conversion has also been observed by treating octaphenylcyclotetrasilane with catalytic amounts of alkali metals.⁹⁴ The proposed mechanism of this reaction is shown in the following reaction sequence. A



(R'M is CM or SiM compounds; R is phenyl; n is 1 or 2)

similar catenation and cyclization reaction is reported in This Thesis, which occurs upon the treatment of octaphenyl-

⁹³(a)A. W. P. Jarvie and H. Gilman, *J. Org. Chem.*, **26**, 1999 (1960); (b)H. Gilman and A. W. P. Jarvie, Chemistry Department, Iowa State University of Science and Technology, Ames, Iowa. Results from cleavage studies on polysilanes, private communication, 1961.

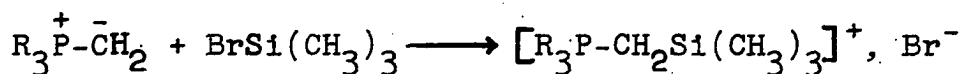
⁹⁴H. Gilman and H. J. S. Winkler, Chemistry Department, Iowa State University of Science and Technology, Ames, Iowa. Results from reactions of polysilanes, private communication, 1960.

cyclotetrasilane with lithium aluminum hydride.

By employing excess organometallic compounds and short reaction periods, organosilylmetallic compounds containing more than one silicon have been obtained. For example, using a 2:1 mole ratio of methyllithium to octaphenylcyclotetrasilane in tetrahydrofuran for 30 minutes, followed by derivatization with methyl phosphate, gave a 69% yield of 1,4-dimethyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane.⁸⁹ Also, pentaphenyldisilanyllithium resulted from the reaction with excess triphenylsilyllithium.^{93a}

The Wittig Reaction^{95,96}

There has been only one reported synthesis of an organosilicon compound by means of the Wittig reagent.⁹⁷ Treatment of bromotrimethylsilane with methylenetriphenylphosphorane resulted in the formation of a phosphonium salt, as illustrated in the following reaction. The isolation and purification of this salt was rendered difficult due to its ready



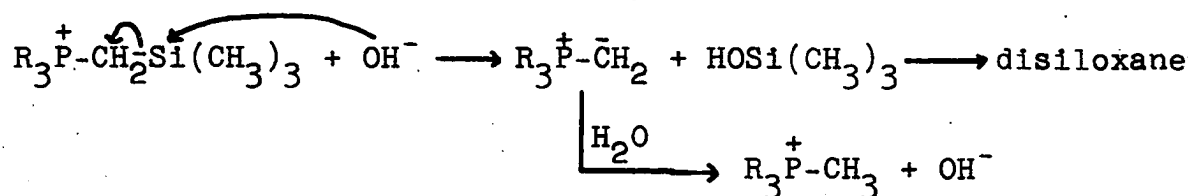
ication of this salt was rendered difficult due to its ready

⁹⁵G. Wittig and U. Schöllkopf, Ber., 87, 1318 (1954).

⁹⁶See also the review by U. Schöllkopf, Angew. Chem., 71, 260 (1959).

⁹⁷D. Seyferth and S. O. Grim, J. Am. Chem. Soc., 83, 1610 (1961).

hydrolysis as shown in the next reaction sequence.⁹⁷ The



cleavage of octaphenylcyclotetrasilane by methylenetriphenylphosphorane is reported in This Thesis. The products obtained were indicative of an intermediate organosilyl-substituted "ylide". Preliminary investigations on the possibility of using such compounds in the synthesis of vinyl-substituted organosilanes were undertaken and are reported herein.

EXPERIMENTAL

General Procedures

All reactions involving substances which would react with oxygen or moisture were carried out in oven-dried glassware under atmospheres of dry, oxygen-free nitrogen. With the exception of tetrahydrofuran, hereafter abbreviated as THF, anhydrous solvents were dried by storage over sodium wire. The THF was dried by refluxing over metallic sodium for at least 24 hr., distillation from the sodium into lithium aluminum hydride, followed by distillation from the lithium aluminum hydride immediately before use. The drying operation was conducted under an atmosphere of oxygen-free, dry nitrogen.

The reaction mixtures were all mechanically stirred. The temperatures recorded are all uncorrected. Melting point and mixed melting point determinations on octaphenylcyclotetrasilane and Compound (B)⁹⁸ were carried out by placing the samples in a block, which had been preheated to about 10° below the reported temperatures, and heating at a rate of about 2° per minute. Infrared spectra were routinely determined on all products. Silicon analyses were carried out

⁹⁸The structure of Compound (B) has been proposed as dodecaphenylcyclohexasilane.^{87,88} However, more recent evidence strongly indicates that it is decaphenylcyclopentasilane.^{82,89,90}

in a manner similar to a published procedure.⁹⁹

The term "usual work-up" used herein refers to the following experimental procedure. The aqueous layer was separated from the organic layer and extracted three times with ca. 75-ml. portions of ether (occasionally benzene), and discarded. The combined extracts and organic layer were washed successively with ca. 50-ml. portions of distilled water until the wash water was neutral to litmus. The organic phase was dried over anhydrous sodium sulphate, and the solvents removed by distillation.

Hydrogenolysis of Organopolysilanes

General procedure for high pressure reactions

The reactions were carried out in a Pyrex container, placed in a one-liter steel bomb, which was heated by an external heater, and agitated by a rocking assembly.¹⁰⁰ In most cases, the volume of the system was decreased by ca. 600 ml. by insertion of an aluminum bar into the bomb and placing a 400-ml. glass liner on top, using coil springs to hold it in position.

The system was flushed two or three times with hydrogen by filling to ca. 800 p.s.i.g., and releasing to atmospheric

⁹⁹H. Gilman, B. Hofferth, H. W. Melvin, and G. E. Dunn, J. Am. Chem. Soc., 72, 5767 (1950).

¹⁰⁰The apparatus was manufactured by the American Instrument Co., Silver Springs, Maryland.

pressure before filling to the desired pressure. Agitation and heating were begun at the same time. About 30 min. were required to reach a temperature of 100°, and approx. 5 min. for each additional 30° rise. The temperature was measured by means of an iron-constantan thermocouple, placed externally in a well in the bottom of the bomb. The temperature was maintained within $\pm 10^\circ$ of that recorded. The duration of heating was measured from the time the reported temperature was reached until the heater was turned off and agitation stopped. Cooling to room temperature usually required about 8 hr. The bomb was washed with ca. 50 ml. of solvent, which was combined with the reaction mixture. The solids were removed by filtration, and washed with a few ml. of solvent. After removal of the solvents by distillation, the products were isolated by crystallization and/or distillation under reduced pressure. The products were identified by their infrared spectra and, in the case of solids, by melting points and mixed melting points with authentic samples; liquids were also identified by their refractive indices.

Octaphenylcyclotetrasilane

Five grams (0.006 mole) of octaphenylcyclotetrasilane was used in each run. Unless otherwise indicated, the reactions were carried out in ca. 100 ml. of a purified grade of cyclohexane, m.p. 5-6°, used without further purification. Due to its insolubility, recovered starting material was usually

identified without separation from the catalyst. There was about 4% of solid,¹⁰¹ m.p. ca. 500°, present in the starting material, which was recovered unreacted. The 1,1,2,2,3,3,4,4-octaphenyltetrasilane was obtained by concentration of the solvent and addition of petroleum ether (b.p. 60-70°). The melting point was usually in the range of 154-160°, which was raised to 161-162° (mixed m.p.) upon recrystallization. The solvents were removed from the mother liquor, and the oily residue distilled under a reduced pressure of about 3 mm., with the diphenylsilane being collected over a 3-4° range at temperatures of about 110°. The refractive indices of all samples collected were within the range of 1.5795⁺ - 0.0005 (reported⁶² n_D^{20} 1.5795). Further distillation at a pressure of 0.005-0.008 mm. and temperatures of around 100°, yielded 6-10% of material, which contained SiH and SiOSi bands in the infrared spectra. Attempts to purify or separate components from this material were unsuccessful. No crystalline products could be isolated from the distillation residues, which also showed strong absorption bands in their infrared spectra due to SiOSi and SiH groups. The reaction conditions and results are given in Table 1.

¹⁰¹This material is formed as a by-product in the preparation of octaphenylcyclotetrasilane, and was labeled "Compound C" by F. S. Kipping.⁸⁴

Table 1. Hydrogenolysis of octaphenylcyclotetrasilane^a

Catalyst	Time, Hr.	Temp., °C.	Pressure, p.s.i.g.	% R_2SiH_2	% $R_8Si_4H_2$ ^b	% Starting Material
none added ^c	2	150	800	-	-	94 ^d
" ^e	4	250	1450	trace ^f	2	86
CuCr ^g	1	150	760	46	8	2
"	2	150	890	42	5	-
"	5	150	800	48	12	2
" ^c	1	150	100	-	4	44
CuO- Cr ₂ O ₃ ^h	1	150	800	14	-	72
"	1	150-260	750-1000	8	-	-
"	3.5	150	975	50	-	-
"	2	150	160	-	-	98
Ni ⁱ	1	150	870	-	-	94
Pd/C(10%) (0.5 g.)	2	150	830	-	-	96
Ce, J	3	150-240	1150-1540	-	-	94 ^d

^aR is phenyl in all cases. In most cases, a siloxane mixture was also obtained and is more fully described in the experimental part.

^b1,1,2,2,3,3,4,4-octaphenyltetrasilane.

^cReagent grade xylene was the solvent used.

^dA trace of soluble material containing SiH absorption bands in its infrared spectrum was also obtained.

^eThe solvent was reagent grade toluene.

^fTrace of material with the odor of diphenylsilane.

^gCuCr is used as the abbreviation for "copper chromite", which was prepared according to the direction of R. Connor, K. Folkers, and H. Adkins, J. Am. Chem. Soc., **54**, 1138 (1932).

^hA mixture of 0.3 g. of CuO and 0.2 g. of Cr₂O₃, which was ground together in a mortar and dried at 130° for 3 hr.

ⁱRaney nickel of W-2 activity. Approx. 1 g. was used.

^jOne gram of Norite "A" charcoal.

Other organopolysilanes

The reactions were carried out as described in the general procedure. The experimental conditions and results are shown in Table 2.

Triphenylsilane

Conversion to hexaphenyldisiloxane under hydrogenolysis conditions Five grams of "copper chromite" catalyst, 5.2 g. (0.02 mole) of triphenylsilane, and 100 ml. of cyclohexane were heated for 3.5 hr. at 150° under 800 p.s.i.g. of hydrogen pressure. After cooling, the catalyst was removed by filtration and washed with benzene. The filtrate and the benzene washings were combined and most of the solvents removed. The addition of petroleum ether (b.p. 60-70°) gave 3.1 g. (60%) of impure hexaphenyldisiloxane, m.p. 216-220°. One recrystallization raised the melting point to 222-224° (mixed m.p.). An infrared spectrum of the material remaining in the mother liquor showed a strong absorption band between 9 and 10 microns, characteristic of siloxane groups; there was no band at 4.7 microns, indicating the absence of material containing the silicon-hydrogen group.

Attempted oxidation with copper (II) oxide A mixture of 5.2 g. (0.02 mole) of triphenylsilane and 3.0 g. (0.01 mole) of copper (II) oxide (dried at 120° for 2 hr.) was refluxed for 24 hr. in dry xylene. (The solvent was dried by storage over sodium and was freshly distilled under oxygen-

Table 2. Hydrogenolysis of other organopolysilanes^a

Compound (g.)	Catalyst (g.)	Time, hr.	Temp., °C.	Pressure p.s.i.g.	Products, (%)
Compound (B) ^b (7.5)	CuCr ^c (0.7)	2	150	850	(C ₆ H ₅) ₂ SiH ₂ , (trace); ^d starting material, (80); polysiloxane ^e
"	"	4	200	1000	starting material, (66); polysiloxane ^e
(C ₆ H ₅) ₆ Si ₂ (5.2)	" (0.5)	2	150	850	(C ₆ H ₅) ₃ SiH, (17); ^f (C ₆ H ₅) ₆ Si ₂ O, (10); ^f starting material, (59.1)

^aThe solvent used in each reaction was ca. 80 ml. of a purified grade of cyclohexane, m.p. 5-6°, used without further treatment.

^bDodecaphenylcyclohexasilane or decaphenylcyclopentasilane.⁹⁸

^c"Copper chromite"; see footnote (g), Table 1.

^dIdentified by its infrared spectrum.

^eAn infrared spectrum on the distillation residue contained a strong absorption band between 9 and 10 microns, indicative of SiOSi groups; attempts to purify this material were unsuccessful.

^fThe triphenylsilane melted at 44-46° (mixed m.p.); the hexaphenyldisiloxane melted at 200-220°, which was raised to 222-225° (mixed m.p.) upon one recrystallization.

Table 2. (Continued)

Compound (g.)	Catalyst (g.)	Time, hr.	Temp., °C.	Pressure p.s.i.g.	Products, (%)
$(C_6H_5)_6Si_2$ (5.2)	$CuCr^c$ (0.5)	5	150	820	$(C_6H_5)_6Si_2O$, (22) starting material, (68) ^g
$[(CH_3)(C_6H_5)_2Si]_2$ (6.0)	"	2	"	810	$(CH_3)(C_6H_5)_2SiH$, (73.2) ^h
$[(CH_3)(C_6H_5)_2Si]_2$ (12.2)	$Ni^i(W-5)$ (1)	8	150- 170	1000- 1220	starting material, (91.2); other products ^j

^gIdentified without separation from the catalyst. Also, an infrared spectrum on the material remaining in the mother liquor did not contain absorption bands for SiH bonds, indicating the absence of any triphenylsilane. The same results were obtained in a second run under similar conditions.

^hB. p. 109-112° (2.3 mm.), n_D^{20} 1.5720; reported, n_D^{20} 1.5717, V. F. Mirnov and A. D. Petrov, Izvest. Akad. Nauk, S.S.S.R., Otdel, Khim. Nauk, 1957, 383; [C. A. 51, 15457 (1957)].

ⁱRaney nickel (W-5); see the hydrogenation of tetraphenylsilane in the experimental part.

^jA ca. 6% yield of material, b.p. 60-80° (0.12 mm.), was obtained, the infrared spectrum of which showed cyclohexyl and/or cyclohexenyl, and SiH groups.

Table 2. (Continued)

Compound (g.)	Catalyst (g.)	Time, hr.	Temp., °C.	Pressure p.s.i.g.	Products, (%)
$[(CH_3)(C_6H_5)_2Si]_2^k$ (11.8)	Ni ¹ (W-5) (3)	11	200- 220	1550- 1650	starting material, (69.4); other products ¹
$[(CH_3)_2(C_6H_5)Si]_2$ (6.0)	CuCr ^c (0.5)	2	150	800	$(CH_3)_2(C_6H_5)SiH^m$ (21.7, impure); mixture of starting material and disiloxane ⁿ (50)
$[(C_6H_5)_2SiH]_2$ (12.2)	Ni(W-2) (1)	3.5	150	800	starting material, (84.4); $(C_6H_5)_2SiH_2$, (trace); siloxane ^e

^kRecovered starting material from the preceding run was used.

¹Material similar to that described in footnote (j) was obtained, except that it contained SiOSi groups instead of SiH groups.

^mThe impure material was collected in four fractions, b.p. 53-64° (20-30 mm.), with the n_D^{20} ranging from 1.4914 to 1.4979; reported n_D^{20} 1.4988, G. A. Russell, J. Org. Chem., 21, 1190 (1956).

ⁿB. p. 77-80° (0.06 mm.), n_D^{20} 1.5436; the infrared spectrum was similar to that of starting material, except that it contained an additional band of medium intensity at 9.4 microns, indicative of disiloxane impurities. This band was not so intense as that in the spectrum of pure disiloxane.

Table 2. (Continued)

Compound (g.)	Catalyst (g.)	Time, hr.	Temp., °C.	Pressure p.s.i.g.	Products, (%)
$(C_2H_5)_6Si_2$ (8.3)	$CuCr^c$ (0.5)	2	150	800	starting material, (90.4) ^o
$(C_6H_5)_6Si_2O$ (10.0)	$CuCr^c$ (0.5)	2	150	800	starting material, (98.4) ^p

^oThe solvent was carefully distilled through a spinning band column, rated at 23 theoretical plates by the manufacturers, Nester and Faust Co. No evidence for any material containing SiH bonds was detected in the spectra on the various fractions of the forerun, which did not boil higher than 66° (triethylsilane boils at 104°).

^pA spectrum on the residue obtained from the mother liquor showed the absence of any material containing SiH or SiOH groups.

free, dry nitrogen. Similarly purified nitrogen was bubbled through the refluxing solvent for 30 min. to remove dissolved oxygen.) There was no color change in the copper oxide, which was removed by filtration. The solvent was removed under reduced pressure at room temperature. The residue was dissolved in petroleum ether (b.p. 60-70°) and passed through a column of activated alumina. Removal of the solvent from the petroleum ether eluate yielded 4.0 g. (78%) of recovered triphenylsilane, m.p. 44-46° (mixed m.p.). The benzene and methanol eluates yielded 0.27 g. (5%) of hexaphenyldisiloxane, m.p. 217-220°. Recrystallization raised the melting point to 222-224° (mixed m.p.).

Hydrogenation of tetraphenylsilane

Tetraphenylsilane was hydrogenated according to published directions⁸ to establish the effectiveness of the Raney nickel (W-5) used in the reactions of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane, described in Table 2, and to insure that the cyclohexane used as solvent did not contain a catalyst poison. A suspension of 16.8 g. (0.05 mole) of tetraphenylsilane and ca. 4 g. of catalyst was heated in 90 ml. of solvent, with the absorption of hydrogen being detected at 100° and 1100 p.s.i.g. pressure. The temperature was raised to 170° for 1 hr. and the system allowed to cool. Another portion of catalyst was added and the mixture heated to 170° for an additional 2 hr. at 1200

p.s.i.g. pressure. The drop in pressure, at rm. temp., was 380 lb. after the first stage, and 110 lb. after the second treatment. The nickel and solids were removed by filtration and treated with excess dilute acid to dissolve the catalyst, leaving 11.6 g. (66.9%) of impure tetracyclohexylsilane, m.p. 260-280°. Two recrystallizations from toluene raised the melting point to 279-281°, the reported m.p.⁸ An NMR spectrum in CDCl_3 (saturated solution at 25°) showed only a complex of bands between 8.1-9.1 τ , with respect to TMS, and did not contain bands due to hydrogen attached to phenyl or carbon-carbon unsaturated sites. An infrared spectrum on the material remaining in the cyclohexane contained a weak absorption band at 4.7 microns, characteristic of Si-H bonds.

Low pressure reactions (attempted)

Several low pressure hydrogenolysis reactions were attempted, from which starting materials were recovered in high yields. No evidence for any reduction products was detected. The results are given in Table 3.

Reactions Involving Metal Hydrides

General procedure

Unless otherwise indicated, the compound and the metal hydride were refluxed in about 100 ml. of solvent for the reported length of time. The subsequent treatment is recorded for each reaction. After acid hydrolysis and the usual work-up, the products were isolated by crystallization

Table 3. Attempted low pressure hydrogenolysis of perphenylated cyclic polysilanes^a

Compound	Time (hr.)	Temp., C°	Pressure, p.s.i.g.	Solvent	Catalyst	% Recovery ^b
R ₈ Si ₄ ^c	3	130	14.7 ^d	xylene	CuCr ^e	94
"	24	50	50	"	"	94.4
"	18	80	53	benzene	10% Pd/C	88
"	24	80	53	THF	Ni ^f	75
Compd. (B) ^g	19	80	50	cyclo-hexane	"	87
"	20	27	51	"	10% Pd/C	98

^aR refers to phenyl. With one exception (see footnote d), the reactions were carried out in a conventional Parr shaking apparatus. No significant pressure changes were noted in any case. Infrared spectra on the residues obtained by evaporating the solvent from the mother liquors did not show absorption bands due to SiH bonds.

^bIn certain cases, the recovery of all of the starting material was rendered difficult by the fact that it tended to climb on the solvent film, and even blocked the valve leading to the reservoir tank.

^cOctaphenylcyclotetrasilane.

^dThe reaction was carried out at one atmosphere of hydrogen pressure, in a Pyrex flask attached to a manometer, in a closed system.

^eThe catalyst was "copper chromite", see footnote (g), Table 1.

^fRaney nickel (W-2).

^gDodecaphenylcyclohexasilane or decaphenylcyclopentasilane.⁹⁸

and/or distillation under reduced pressure.

Lithium aluminum hydride reactions

Hexaphenyldisilane in tetrahydrofuran The reactions were carried out as described in the general procedure in refluxing tetrahydrofuran. In one case, the grey lithium aluminate present in the lithium aluminum hydride was removed by filtration of the THF solution through a sintered glass funnel prior to the addition of hexaphenyldisilane; an almost clear, light yellow solution resulted after 24 hr. of reflux.

From some reactions, subsequent to hydrolysis, hexaphenyldisilane was recovered by filtration prior to the usual work-up. In most cases, the triphenylsilane was isolated by distillation under reduced pressure and usually melted at 44-46° (mixed m.p.). The material remaining in the distillation residue could not be purified; its infrared spectrum showed strong absorption bands due to SiOH and SiOSi groups. In the distillation of the triphenylsilane, there was usually obtained a small amount of low boiling material. On occasion, it was isolated in sufficient quantity to be identified as diphenylsilane. The experimental conditions and results are given in Table 4.

Infrared analyses of mixtures of triphenylsilane and triphenylsilane-d were carried out on a Perkin Elmer "Model 21" double beam spectrophotometer using a 0.5 mm., sodium

Table 4. Cleavage of hexaphenyldisilane by lithium aluminum hydride in THF^a

Grams (C ₆ H ₅) ₆ Si ₂	Hours reflux	Treatment	% Yield (C ₆ H ₅) ₃ SiH ^b	Other products ^c	%
5.2	48	reflux 1 hr. with excess (CH ₃) ₃ SiCl; acid hydrolysis	60	--	--
10.4	72	acid hydrolysis	65.6	(C ₆ H ₅) ₂ SiH ₂	3
"	24	carbonation; ^d acid hydrolysis	62.0 ^e	(C ₆ H ₅) ₆ Si ₂	10
"	60	"	60.1	(C ₆ H ₅) ₂ SiH ₂	2

^aThe reactions were carried out as described in the experimental part, with the mole ratio of reactants being 1:1 in each case.

^bYield based on two moles of product from one mole of disilane.

^cIn addition to the products listed, distillation residues yielded varying amounts of viscous oils, which resisted attempts to purify. The infrared spectra indicated the presence of SiOH and SiOSi groups.

^dCarbonation was accomplished by pouring the reaction mixture onto a slurry of Dry Ice and ether, and allowing the mixture to warm to room temperature before hydrolyzing.

^eThe yield was based on unrecovered starting material.

Table 4. (Continued)

Grams (C ₆ H ₅) ₆ Si ₂	Hours reflux	Treatment	% Yield (C ₆ H ₅) ₃ SiH ^b	Other products ^c	%
6.2	24	(lithium aluminum deuteride was used) hydrolyzed in H ₃ O ⁺	31 ^f (62) ^g	(C ₆ H ₅) ₃ SiD	44.3 ^f (88.6) ^g
10.4	96	reflux with excess (CH ₃) ₃ SiCl; hydro- lyze in D ₃ O ⁺	47 ^{e,f} (94) ^g	(C ₆ H ₅) ₃ SiD (C ₆ H ₅) ₆ Si ₂	31 ^{e,f} (62) ^g 36.5

^fSee the experimental part for the analysis of the mixture of (C₆H₅)₃SiH and (C₆H₅)₃SiD.

^gThe yield in parentheses is based on one mole of disilane forming one mole each of (C₆H₅)₃SiH and (C₆H₅)₃SiD.

chloride cell. The samples were analyzed for triphenylsilane-d using the absorption band at 6.45 microns, which is characteristic of silicon-deuterium bonds.¹⁰² The solvent was Eastman spectral grade bromoform. The results were an average of at least three determinations. The spectra were run at 25°. The base line was corrected for background by using a line drawn between the two minimum points on either side of the band. The absorbency of the solute was determined by measuring the % transmission at the base line, and at the maximum, converting to logarithms and subtracting. Standard solutions of triphenylsilane-d were prepared with concentrations ranging from 6 to 40 mg./ml. Conformity with Beer's law was established by the standardization plot, which was a good straight line, nearly passing through the origin. The analysis of a prepared mixture containing 12.2 mg. of triphenylsilane-d and 40.0 mg. of triphenylsilane per ml. gave 12.8 mg./ml., a value 5% higher than the theoretical. The amount of triphenylsilane in the mixture was calculated by subtracting the quantity of triphenylsilane-d from the total weight of the sample. The results are reported with each individual experiment.

Hexaphenyldisilane in diethyl ether (attempted) A
suspension of 10.4 g. (0.02 mole) of hexaphenyldisilane and

¹⁰²R. N. Kniseley, V. A. Fassel, and E. E. Conrad, Spectrochim. Acta, 13, 651 (1959).

0.76 g. (0.02 mole) of lithium aluminum hydride was refluxed in ca. 100 ml. of ether for seven days. The reaction mixture was hydrolyzed in a mixture of excess dilute acid and crushed ice. Filtration of the insoluble material gave 10.3 g. (99.2%) of recovered starting material, m.p. 364-367° (mixed m.p.). Similar results have previously been reported after refluxing for 48 hr.²⁹

Hexaphenyldisilane in pyridine (attempted)

Run 1 A mixture of 5.2 g. (0.01 mole) of hexaphenyldisilane and 0.38 g. (0.01 mole) of lithium aluminum hydride was stirred at room temperature for 48 hr. in 30 ml. of pyridine (dried over barium oxide). The brown mixture was slowly poured onto crushed ice containing 30 ml. of concentrated hydrochloric acid. The solids were filtered, washed with ether, water, and dried to give 5.0 g. (96%) of recovered starting material, m.p. 365-367° (mixed m.p.).

Run 2 The experiment was carried out in a manner similar to that described in Run 1, except that the mixture was heated at 60-70° for 72 hr. Subsequent to hydrolysis, there was obtained 5.0 g. (96%) of recovered starting material, m.p. 364-366° (mixed m.p.).

Run 3 The reaction was carried out as in the other two cases, except that the mixture was refluxed for 54 hr. Work-up yielded 95% of recovered starting material.

Triphenylsilane in THF A mixture of 10.0 g. (0.04 mole) of triphenylsilane (free of di- and tetraphenylsilane)

and 1.5 g. (0.04 mole) of lithium aluminum hydride was refluxed in ca. 100 ml. of THF for 46 hr. Subsequent to acid hydrolysis and the usual work-up, the products were distilled under reduced pressure to give 0.2 g. (2.8%) of impure diphenylsilane, b.p. 60-70° (0.15 mm.), n_D^{20} 1.5828 (lit. value⁶² 1.5795), identified by its infrared spectrum and its characteristic odor. Further distillation gave 8.5 g. (85%) of recovered triphenylsilane, b.p. 125-129° (0.15 mm.), m.p. 44-46° (mixed m.p.). The distillation residue partially solidified on cooling. The solid material was washed with petroleum ether (b.p. 60-70°) and then recrystallized from ethyl acetate to give 0.2 g. (1.5%) of tetraphenylsilane, m.p. 232-235° (mixed m.p.).

Similar results were obtained from a second run under the same conditions.

Triphenylsilane and lithium aluminum deuteride in THF

A mixture of 5.2 g. (0.02 mole) of triphenylsilane and 0.84 g. (0.02 mole) of lithium aluminum deuteride was refluxed in 65 ml. of THF for 24 hr. The mixture was hydrolyzed in a mixture of crushed ice and excess dilute acid. Subsequent to the usual work-up, the products were distilled under reduced pressure to give 0.1 g. (2.8%) of impure diphenylsilane (identified by its infrared spectrum and its characteristic odor), b.p. 40-50° (0.17 mm.), and 4.1 g. (78%) of triphenylsilane, b.p. 125-130° (0.17 mm.), m.p. 42-45° (mixed m.p.). The infrared spectra of these

materials contained strong absorption bands for both silicon-hydrogen and silicon-deuterium bonds. From the distillation residue, there was obtained 0.1 g. (1.5%) of tetraphenylsilane, m.p. 232-235° (mixed m.p.).

Tetraphenylsilane in THF (attempted) A solution of 10.0 g. (0.03 mole) of tetraphenylsilane and 1.5 g. (0.04 mole) of lithium aluminum hydride in 100 ml. of THF was refluxed for 89 hr. The reaction mixture was poured onto a slurry of Dry Ice and ether. After allowing the carbonation mixture to warm to room temperature, dilute acid was added, and the solids filtered off. The solids were washed with ether and dried to give 9.3 g. (93%) of recovered starting material, m.p. 234-236° (mixed m.p.). The ether washings were combined with the filtrate, which was then made basic with sodium hydroxide. The organic layer was separated and washed three times with 75-ml. portions of 5% sodium hydroxide solution. The aqueous layer was acidified with conc. hydrochloric acid, and extracted four times with 75-ml. portions of ether. Evaporation of the ether gave only a trace of solid, m.p. 222-228°, identified as impure tetraphenylsilane by its infrared spectrum. An additional 0.3 g. (3%) of tetraphenylsilane was obtained from the original organic layer.

Other organodisilanes in THF The reactions were run as described in the general procedure, using a 1:1 mole ratio of reactants in each case. The reaction conditions and

results are listed in Table 5.

Hexaethyldisilane (attempted) The reaction was carried out as described in the general procedure, using 12.5 g. (0.054 mole) of hexaethyldisilane and 2.0 g. (0.054 mole) of lithium aluminum hydride in 100 ml. of THF. The reaction mixture was refluxed for 67 hr. and hydrolyzed by pouring onto a mixture of crushed ice and excess dilute acid. Subsequent to the usual work-up, the solvents were carefully fractionated through a spinning band column, rated by the manufacturers at 23 theoretical plates. Although the pot temperature was raised to 150° and the column temperature to 125°, no material boiling higher than 65° was obtained (triethylsilane boils at 104°). Infrared spectra on the various fractions of forerun did not show any absorption bands due to SiH bonds. Distillation of the residue under reduced pressure gave 9.1 g. (72.8%) of recovered starting material, b.p. 87-90° (1.9-2.0 mm.), n_D^{20} 1.4790 (the reported¹⁰³ refractive index).

A second run was carried out with the same quantities of starting materials. The reaction mixture was refluxed for 65 hr., during which a trap, cooled by a slurry of Dry Ice and acetone, was attached to the end of the reflux

¹⁰³M. G. Voronkov and Y. I. Khudobin, Zhur. Obshchei Khim., 26, 584 (1956); [Original available but not translated; translated in J. Gen. Chem. U.S.S.R., 26, 629 (1956)].

Table 5. Cleavage of organodisilanes by lithium aluminum hydride in THF

Compound (g.)	Hours reflux	Treatment	Products	%
$(C_6H_5)_6Si_2^a$ (10.4)	72	acid hydrolysis	$(C_6H_5)_3SiH$	60
$[(CH_3)(C_6H_5)_2Si]_2$ (6.0)	67	"	$(CH_3)(C_6H_5)_2SiH^b$	40
$[(CH_3)_2(C_6H_5)Si]_2$ (10.0)	65	"	$(CH_3)_2(C_6H_5)SiH$, (impure); ^c $[(CH_3)_2(C_6H_5)Si]_2$	23 41.5
$(CH_3)_3SiSi(C_6H_5)_3$ (6.0)	61	carbon- ation, acid hydrolysis	$(CH_3)_3SiH$; ^d $(C_6H_5)_3SiH$; $(C_6H_5)_3SiOH$	50 63.9 14
$(C_2H_5)_6Si_2$	65-67	-- ^e	$(C_2H_5)_3SiH$ $(C_2H_5)_6Si_2$	0 72.8

^aA representative sample; see Table 4 for more complete information.

^bB. p. 107-110° (2.3 mm.), n_D^{20} 1.5717 (see footnote h, Table 2).

^cCollected in three fractions, b.p. 50-70° (50-70 mm.), with n_D^{20} values ranging from 1.4928-1.4988 (see footnote m, Table 2).

^dCollected prior to hydrolysis by means of a trap cooled to -65°, which was attached to the end of the reflux condenser. Identification was made by its infrared spectrum as solutions in carbon disulfide and carbon tetrachloride.

^eThe results of two runs. See the experimental part for details.

condenser. An infrared spectrum on the small amount of material collected did not show the presence of triethylsilane. The reaction mixture was treated with excess chlorotriphenylsilane, and refluxed for 1 hr. Most of the solvent was removed under a pressure of 10 mm., with the distillate being collected in a trap at -65° . The remainder of the low-boiling substances was removed at a pressure of 0.02 mm. and collected in a trap cooled with liquid nitrogen. Fractionation of the combined distillates, as described in the first run, did not yield any products showing silicon-hydrogen absorption bands in their infrared spectra. The reaction mixture was hydrolyzed in excess dilute acid and, subsequent to the usual work-up, yielded no products boiling higher, at atmospheric pressure, than the ether used in the work-up. During the distillation under reduced pressure, a mechanical loss of some of the products was incurred due to bumping. Distillation afforded 6.25 g. (50.0%) of recovered starting material, b.p. $85-87^{\circ}$ (1.5 mm.), n_D^{20} 1.4781 (reported n_D^{20} 1.4790).¹⁰³

Perphenylated organopolysilanes All of the reactions were run in about 100 ml. of THF. The reaction conditions and results are given in Table 6. Some representative reactions are described in the following sub-paragraphs with the results also appearing in Table 6.

Octaphenylcyclotetrasilane A mixture of 10.0 g. (0.014 mole) of octaphenylcyclotetrasilane and 0.14 g.

Table 6. Cleavage of perphenylated organopolysilanes by lithium aluminum hydride in THF

Compound ^a (g.)	Mole ratio cmpd.: LiAlH ₄	Hours reflux	% Yield of R _{2n} Si _n H ₂ ^a n equals					Other products	%
			1	2	3	4	5 ^b		
R ₈ Si ₄ ^c (10)	4:1	- ^d	- ^e	- ^e	-	3	-	Cmpd. (B) ^f	64
"	"	- ^d	- ^e	- ^e	-	6	-	"	62
" (7.3)	1:1	1.5	- ^e	- ^e	-	16.5	8.2	"	16.5
Cmpd. (B) ^f (10.9)	4:1	0.2 ^g	- ^e	- ^e	-	6	-	"	74

^aR is phenyl.

^bThe structure of this material has been proposed as a hexasilane.⁹⁴ However, more recent evidence from This Laboratory indicates it to be a pentasilane.⁸²

^cOctaphenylcyclotetrasilane.

^dThe reaction mixture was stirred at room temperature for 20 hr.

^eNo attempt was made to isolate these materials.

^fDodecaphenylcyclohexasilane or decaphenylcyclopentasilane.⁹⁸ The mole ratio is based on a hexasilane.

^gRefluxed for 12 min. after stirring at room temperature for 18 hr.

Table 6. (Continued)

Compound ^a (g.)	Mole ratio cmpd.: LiAlH ₄	Hours reflux	% Yield of R _{2n} Si _n H ₂ ^a n equals					Other products	%
			1	2	3	4	5 ^b		
Cmpd. (B) ^f (10.9)	1:1	41	- ^e	10	-	7	-	Cmpd. (B) ^f	9
"	"	1.5	- ^e	2	1	5	2	"	68
"	1:2	44	16 ^h	34	-	10	-		
R ₈ Si ₄ Cl ₂ (9.1)	1:1	24	12 ^h	26	14.4	14			
R ₈ Si ₄ H ₂ (2)	1:1	2	7.5 ^h	10	30	5			

^hObtained on distillation under reduced pressure.

(0.0037 mole) of lithium aluminum hydride was stirred at room temperature for 20 hr. in a suspension of ca. 100 ml. of THF. The reaction mixture was a light yellow color. In an attempt to derivatize any silylmetallic compound present, a solution of 2.8 g. (0.02 mole) of trimethyl phosphate in 25 ml. of THF solution was added in a dropwise fashion. The yellow color faded after the addition of the first few ml. After the addition was completed, the reaction mixture was hydrolyzed in a mixture of excess dilute acid and crushed ice. Subsequent to the usual work-up, and removal of the solvents, the residue was dissolved in a small amount of benzene, heated to reflux, and petroleum ether (b.p. 60-70°) was added. Upon cooling, 6.7 g. (66.5%) of Compound (B)⁹⁸ was obtained, m.p. 450-455° (mixed m.p.). Removal of solvent from the mother liquor gave an oil which, when treated with cold petroleum ether (b.p. 60-70°), partially solidified and was filtered to give 1.3 g. (13%) of material, m.p. 153-159°, (with sintering at 140°, and the melt not being clear even to 200°). This material was dissolved in a few drops of benzene, and hot petroleum ether added. On cooling, 0.8 g. (8%) of solid was obtained, with no appreciable change in melting point. The material was fractionally crystallized from ethyl acetate. The first fraction, 0.2 g. (2%) melted over the range of 300-350° (cloudy). The second fraction, 0.3 g. (3%) melted 160-162° and was identified as 1,1,2,2,3,3,4,4-octaphenyltetrasilane by its infrared spectrum

and a mixed melting point determination. No product containing a silicon-methyl group was isolated, nor was there any evidence for this group in the infrared spectrum on the oily residue obtained by removal of the solvents from the mother liquor. The spectrum did indicate the presence of SiH and SiOSi groups.

Compound (B)⁹⁸ A mixture of 10.9 g. of Compound (B)⁹⁸ (0.01 mole, based on dodecaphenylcyclohexasilane) and 0.38 g. (0.01 mole) of lithium aluminum hydride was refluxed in ca. 100 ml. of THF for 41 hr. Subsequent to acid hydrolysis in the presence of crushed ice, the usual work-up, and removal of the solvents, the residue was dissolved in a small amount of benzene and treated with 100 ml. of hot petroleum ether (b.p. 60-70°). Upon cooling, there was obtained 3.4 g. (31.5%) of material, m.p. 158-166° (with sintering at 150°, and not melting to a clear liquid). Two recrystallizations from the same mixture of solvents did not appreciably alter the melting point. The material was fractionally recrystallized from ethyl acetate. The first fraction was 0.53 g. (4.9%) of starting material, m.p. 445-450° (mixed m.p.). An additional 0.45 g. (4.1%) was obtained from the second fraction. The solvents were removed from the mother liquor, leaving an oily residue which was soluble in cold petroleum ether (b.p. 60-70°). The infrared spectrum of this material showed the presence of SiH and SiOSi groups and the absence of silanols. The material was chroma-

tographed on alumina. The petroleum ether (b.p. 60-70°) eluate yielded 1.3 g. (12%) of crystals, m.p. 63-75°. Recrystallization from ethanol gave 1.1 g. (10%) of pure 1,1,2,2-tetraphenyldisilane, m.p. 80-81° (mixed m.p.).

On standing and partial evaporation, the original mother liquor deposited 1.4 g. (12.8%) of solid, m.p. 144-148° (cloudy). Fractional recrystallization from ethyl acetate gave 0.76 g. (7%) of pure 1,1,2,2,3,3,4,4-octaphenyltetrasilane m.p. 160-162° (mixed m.p.).

Triphenylsilyllithium and lithium aluminum hydride

One to one mole ratio Triphenylsilyllithium was prepared in THF from 15.6 g. (0.03 mole) of hexaphenyldisilane and excess lithium. The brown solution was decanted away from the lithium and added slowly to 2.3 g. (0.06 mole) of lithium aluminum hydride in tetrahydrofuran. The resulting purple solution was stirred at room temperature for 3 hr. and divided in half; one portion was poured slowly upon a slurry of Dry Ice and ether and hydrolyzed with excess dilute acid. To the remaining half, a solution of 17.4 g. (0.16 mole) of chlorotrimethylsilane in 60 ml. of ether was added slowly. The purple coloration faded upon addition of ca. one-third of the solution. The mixture was stirred overnight, refluxed for 1 hr., and hydrolyzed in excess dilute acid.

From the portion of the reaction mixture which was carbonated, there was obtained, subsequent to the usual

work-up and distillation under reduced pressure, 6.1 g. (78.4%) of triphenylsilane, b.p. 135-140° (0.18 mm.), m.p. 42-44° (mixed m.p.).

Subsequent to the usual work-up and removal of solvents, petroleum ether was added to the residue from that portion of the reaction mixture which was treated with chlorotrimethylsilane, to give 0.2 g. (2.4%) of impure triphenylsilanol, m.p. 130-140° (identified by its infrared spectrum). Attempts to isolate any 1,1,1-trimethyl-2,2,2-triphenyldisilane were unsuccessful. The material was distilled under reduced pressure to give 5.3 g. (68%) of triphenylsilane, b.p. 128-132° (0.1 mm.), m.p. 41-44° (mixed m.p.).

Attempts to obtain crystalline products from the distillation residue were unsuccessful. Infrared analysis indicated the presence of silanol and siloxane groups in both cases.

The total yield of triphenylsilane from both portions of the reaction mixture was 73.1%.

Two to one mole ratio A tetrahydrofuran solution of triphenylsilyllithium, prepared from 10.4 g. (0.02 mole) of hexaphenyldisilane and excess lithium, was added to 0.76 g. (0.02 mole) of lithium aluminum hydride in THF. The purple-colored reaction mixture was allowed to stir for 72 hr. at room temperature, prior to pouring onto a slurry of Dry Ice and ether. Subsequent to acid hydrolysis and the usual work-up, the products were distilled

under reduced pressure to give 4.4 g. (43%) of triphenylsilane, b.p. 140-147° (0.25 mm.), m.p. 40-42°. The melting point was raised to 44-46° (mixed m.p.) upon recrystallization from methanol. No crystalline products could be isolated from the distillation residue, the infrared spectra of which showed strong absorption bands characteristic of siloxane and silanol groups.

Triphenylsilyllithium and lithium aluminum deuteride

A solution of triphenylsilyllithium prepared by lithium cleavage of 2.6 g. (0.005 mole) of hexaphenyldisilane in THF was added slowly to a tetrahydrofuran solution of 0.2 g. (0.005 mole) of lithium aluminum deuteride. The reddish-brown solution was stirred at room temperature for 7 hr. and hydrolyzed in a mixture of crushed ice and excess dilute acid. Subsequent to the usual work-up and removal of solvents, the products were distilled under reduced pressure to give 0.9 g. (34.6%) of triphenylsilane, b.p. 120-127° (0.1 mm.), m.p. 42-44° (mixed m.p.). Infrared analysis indicated that 12.5% of the triphenylsilane was deuterated. The infrared spectrum of the material remaining in the distillation residue showed absorption bands indicative of silanol and siloxane groups.

Cleavage of octaphenylcyclotetrasilane by lithium aluminum triphenylsilyl hydride complexes

Method 1 A filtered solution of 0.38 g. (0.01 mole)

of lithium aluminum hydride in 25 ml. of THF was refluxed with 5.2 g. (0.01 mole) of hexaphenyldisilane for 18 hr. A light yellow solution resulted with only a small amount of insoluble material present, which did not decrease after an additional 8 hr. of refluxing. To the solution, at room temperature, there was added 7.3 g. (0.01 mole) of octaphenylcyclotetrasilane (dried at 130° for 12 hr.). The mixture turned a light brown color within a few min. After stirring for 36 hr. at room temperature, the mixture was hydrolyzed in crushed ice containing excess dilute acid. The solids were filtered, washed with benzene, and dried to give 3.3 g. (45.2%) of recovered octaphenylcyclotetrasilane, m.p. 318-321° (mixed m.p.). The combined benzene extract and organic layer were worked up in the usual manner. Subsequent to removal of solvents, the residue was dissolved in a small amount of benzene and hot petroleum ether (b.p. 60-70°) added to give on cooling, 2.2 g. (55%, based on unrecovered starting material) of Compound (B), m.p. 454-460° (mixed m.p.). The solvents were removed from the mother liquor, the residue treated with petroleum ether and the insoluble material filtered to give 0.5 g. of solid, m.p. 140-150° (cloudy). Attempts to purify this material were without success. The solvent was removed from the petroleum ether filtrate and the residue distilled under reduced pressure to give 2.7 g. (52%) of triphenylsilane, b.p. 140-143° (0.35 mm.), m.p. 41-43° (mixed m.p.). The

yield was based on the hexaphenyldisilane used. Attempts to separate the material remaining in the distillation residue by chromatography on alumina gave only small fractions of materials in the petroleum ether (b.p. 60-70°), cyclohexane, and benzene eluates; these materials could not be purified.

Method 2 To a THF solution of aluminum hydride, prepared¹⁰⁴ from 0.57 g. (0.015 mole) of lithium aluminum hydride and 0.66 g. (0.005 mole) of freshly sublimed aluminum chloride, there was added a solution of triphenylsilyl-lithium, obtained from the lithium cleavage of 5.2 g. (0.01 mole) of hexaphenyldisilane in THF. The light yellow solution was allowed to stir for 1 hr., followed by the addition of 14.6 g. (0.02 mole) of octaphenylcyclotetrasilane. The resulting light brown mixture was stirred at room temperature for 30 hr. and hydrolyzed in a mixture of excess acid and crushed ice. The solids were filtered, washed with benzene, and dried to give 1.7 g. (11.7%) of recovered octaphenylcyclotetrasilane, m.p. 320-322°, (mixed m.p.). The other reaction products were worked up as described in Method 1 to give 6.3 g. (48.8%, based on unrecovered starting material) of Compound (B), m.p. 458-462° (mixed m.p.); and 1.6 g. (30.8%) of triphenylsilane, b.p. 140-143° (0.35 mm.), m.p. 42-44° (mixed m.p.). Attempts to separate and purify other products were unsuccessful.

¹⁰⁴E. Wiberg, Angew. Chem., 65, 16 (1953).

Attempted reductions with other metallic hydrides

Various other metallic hydrides were used in attempts to effect silicon-silicon bond reductions. The reagents, reaction conditions, and results are listed in Table 7. The reaction mixtures were all hydrolyzed in crushed ice containing dilute acid. Any remaining solids were filtered off, washed with benzene and dried. The soluble materials were worked up in the usual manner.

Attempted Reductive Cleavages by Various Reducing Agents

A number of common reducing agents employed in organic chemistry was used in attempts to cleave the silicon-silicon bonds in octaphenylcyclotetrasilane and Compound (B).⁹⁸ In most cases starting material was recovered in high yields. The reagents, reaction conditions, and results are listed in Table 8. Infrared analyses on the small amounts of residues remaining in the mother liquors showed no evidence of material containing silicon-hydrogen groups; in most cases, there was a band between 9 and 10 microns, characteristic of siloxane linkages.

Reactions with Metals

Cleavage reactions

Hexaphenyldisilane by lithium in the presence of methyl phosphate It was established that methyl phosphate would not react appreciably with lithium in THF at room temperature in the following manner. A few ml. of a solution of 7.0 g.

Table 7. Attempted reduction of perphenylated cyclic polysilanes with metallic hydrides^a

Compound (g.)	Reducing agent	Reaction conditions	% starting material	Products ^b	%
R ₈ Si ₄ (10)	LiAlH ₄	reflux 7 days in ether	98.7		
"	NaH	reflux 20 hr. in THF	0	Cmpd. (B)	77
"	LiH	reflux 72 hr. in THF	88	"	3
"	NaBH ₄	reflux 5 days in dioxane	64 ^c	siloxane ^b	ca. 20
"	NaH/AlCl ₃	reflux 72 hr. in THF	97		
"	LiAlH ₄ /3 2AlCl ₃	reflux 6 days in THF	95		
Cmpd. (B) (10.9)	LiAlH ₄	reflux 6 days in ether	99		
"	NaH	reflux 18 hr. in THF	93.2		
"	LiH	reflux 72 hr. in THF	92.8		
"	NaBH ₄	reflux 5 days in dioxane	96		
"	LiAlH ₄ /3 2AlCl ₃	reflux 25 hr. in THF	95.8		

^aR is phenyl in all instances. The mole ratio of reactants was 1:1 in each case; in the case of Compound (B), the ratio is based on dodecaphenylcyclohexasilane.⁹⁸

^bThe infrared spectrum of the remaining material, m.p. range 170-190°, showed bands characteristic of siloxane groups, but no silicon hydrogen groups. Material having a similar m.p. range and infrared spectrum was also obtained during an attempted recrystallization of octaphenylcyclotetrasilane from boiling dioxane.

Table 8. Attempted reductive cleavages of perphenylated cyclic organopolysilanes by various reducing agents.

Compound ^a	Reducing agent	Mole ratio, compound: red. ag.	Reaction conditions	% Recovery
R ₈ Si ₄	Zn(Hg)/HCl	7:100	reflux until H ₂ evol. ceased (16 hr.) in a suspension of conc. HCl, toluene, and dioxane	90
Cmpd. (B)	"	"	"	98
R ₈ Si ₄	3% Na(Hg)/HC ₂ H ₃ O ₂	1:10	rm. temp. until H ₂ evol. ceased (8 hr.)	98
Cmpd. (B)	"	"	"	90
R ₈ Si ₄	HI/P(red)	1:2	reflux in xylene for 64 hr.	0 ^b
Cmpd. (B)	"	"	"	71 ^b
R ₈ Si ₄	Al(<u>1</u> -OC ₃ H ₇) ₃	1:1	reflux 48 hr. in benzene	96
"	"	"	reflux 48 hr. in THF	97

^aThe R groups are all phenyl. Five grams of compound was used in each case.

^bThere was a considerable amount of material admixed with the red phosphorus, which was insoluble in organic solvents. An infrared spectrum as a KBr pellet showed no absorption bands for organic groups. The material was apparently a mixture of silica and silicic acid. Refluxing octaphenylcyclotetrasilane with conc. HI in xylene for 64 hr. produced a similar material which was analyzed for silicon. Anal. calcd. for SiO₂: Si, 46.72. Found: 42.39, 41.11.

(0.05 mole) of freshly distilled methyl phosphate in 70 ml. of THF was added to 2.5 g. (0.28 g. atom) of lithium cut into pieces about 5 mm. in length. No reaction was apparent after 15 minutes of stirring. A small crystal of iodine was added and the mixture stirred until the iodine color disappeared. The remainder of the solution of methyl phosphate was added slowly over a two hr. period and the resulting mixture stirred for 48 hr. Color Tests I, taken periodically, were negative. The solution was decanted from the lithium, the solvent removed by distillation, and the residue distilled under reduced pressure to give 6.0 g. (85.7%) of recovered methyl phosphate, b.p. 80-83° (13 mm.).

A mixture of 5.2 g. (0.01 mole) of hexaphenyldisilane, 1.0 g. (0.14 g. atom) of lithium pieces, 6.1 g. (0.043 mole) of methyl phosphate, and 2 ml. of THF was stirred rapidly for 30 min., whereupon the mixture became quite hot. Subsequent to cooling to room temperature, 25 ml. of THF was added slowly and the resulting mixture stirred at room temperature for 8 hr. without evidence of further reaction. On stirring overnight, the reaction mixture turned a very dark, violet color and gave a positive Color Test I.⁷⁵ The reaction mixture was filtered and the filtrate hydrolyzed in excess dilute acid. The excess lithium metal was mechanically separated from the remaining solids, which were then washed with ether, methanol, dilute acid, and distilled water to give, subsequent to drying, 1.1 g.

(21.2%) of recovered hexaphenyldisilane, m.p. 362-365° (mixed m.p.). The organic layer was worked up in the usual manner and yielded an oil after removal of solvents. Attempts to crystallize this material were unsuccessful; it was distilled under reduced pressure to give 0.7 g. of material, b.p. 90-140° (11 mm.), the infrared spectrum of which indicated the presence of methylphenyl-substituted organosilicon hydrides. Further distillation gave 1.2 g. (25%) of impure methyltriphenylsilane, b.p. 120-135° (0.15 mm.), m.p. 63-67°. Recrystallization from methanol gave 0.7 g. (13%) of pure product, m.p. 67-68° (mixed m.p.).

Reaction with chlorotriphenylsilane The reaction was carried out as described in the preceding experiment. The re-initiation occurred during the night, subsequent to 10 hr. stirring. A solution of 12.0 g. (0.04 mole) of chlorotriphenylsilane in 25 ml. of THF was added to the dark reaction mixture. Color Test I was negative after the addition. Work-up as described in the preceding experiment afforded 0.3 g. (2.8%) of hexaphenyldisilane, m.p. 360-364° (mixed m.p.). Triphenylsilanol and hexaphenyldisiloxane were also obtained, which accounted for 75% of the chlorotriphenylsilane used. The residue was chromatographed on alumina. On evaporation, the petroleum ether (b.p. 60-70°) eluate yielded an oil which was distilled under reduced pressure to give a number of fractions boiling over the range 120-150° (13 mm.) and totalling 1.2 g.

The infrared spectra of these fractions indicated the presence of methyl- and phenyl-silicon groups. Further distillation yielded 1.1 g. (22%) of impure methyltriphenylsilane, b.p. 140-148° (0.3 mm.), m.p. 60-65°. Recrystallizations from methanol gave 0.7 g. (13%) of pure product, m.p. 66-67° (mixed m.p.).

The reaction was attempted without using THF. Although a slight warming of the mixture occurred, after 4 days stirring hexaphenyldisilane was recovered in a 95% yield.

Magnesium (attempted) A number of attempted cleavages of organopolysilanes by magnesium and by a mixture of magnesium and magnesium iodide or bromide was carried out. No evidence of cleavage products was detected and starting materials were recovered in high yields. The reactants, reaction conditions, and results are listed in Table 9.

Hexaphenyldisilane by aluminum (attempted) A mixture of 5.2 g. (0.01 mole) of hexaphenyldisilane and 1.0 g. (0.04 g. atom) of aluminum (freshly turned and collected in dry toluene) was refluxed for 5 days in 100 ml. of THF. The reaction mixture was poured into excess dilute acid. After the evolution of hydrogen stopped, the remaining solids were filtered, washed with distilled water, and dried to give 5.15 g. (99%) of recovered material, m.p. 364-366° (mixed m.p.).

Table 9. Attempted cleavages of organopolysilane by magnesium^a

Compound (g.)	Metal system	Reaction conditions	% recovery
R_8Si_4 (5.0)	Mg ^b	reflux for 5 days in THF	96
" (7.3)	Mg/MgI ₂ ^c	stir at rm. temp. for 6 hr., and reflux for 24 hr. in diethyl ether	96
"	" ^{c,d}	reflux for 30 hr. in THF	90.5
R_6Si_2 (5.2)	" ^c	reflux for 2 hr. in diethyl ether after stirring at rm. temp. for 6 hr.	96.5
"	" ^{c,d}	stir with a few ml. of THF for 1 hr., reflux for 1.5 hr., stir overnight at rm. temp., and reflux for 4 hr., followed by the addition of 60 ml. of THF and refluxing for 24 hr.	99
(MDBS) ₂ ^e (1.3)	Mg/MgBr ₂ ^{d,f}	reflux for 48 hr. in THF	84.5

^aR is phenyl. The ratio of g. atom of magnesium to mole of compound was greater than 10:1 in all cases.

^bPowdered magnesium, which had been washed with dilute hydrochloric acid, ethanol, and ether, and dried in an oven at 130° for 3 hr. was used.

^cPrepared by the reaction of iodine and magnesium turnings in ether, in a 1:2 g. atom ratio, respectively.

^dThe ether was removed by distillation from THF.

^e(MDBS)₂ is an abbreviation for 5,5'-dimethyl-5,5'-bi-(dibenzosilole).

^fPrepared by the slow addition of bromine in ether to a cold suspension of magnesium turnings in ether, using a 1:2 g. atom ratio, respectively.

Reactions with organosilicon halidesDichloromethylphenylsilane and lithium To 13.9 g.

(2 g. atoms) of lithium wire pieces, there was added a few ml. of a solution of 191 g. (1 mole) of dichloromethylphenylsilane in 200 ml. of THF. After initiation with a small amount of hexaphenyldisiloxane, the remainder of the solution was added at a rate which maintained a gentle reflux and a slight yellow coloration of the reaction mixture. The rate of reaction slowed down considerably during the addition, with the last 50 ml. of solution requiring 40 min. The total addition time was 2 hr. There was some lithium remaining even after stirring overnight. Subsequent to acid hydrolysis and the usual work-up, only small amounts of solids were obtained which melted over the range 200-240°. Attempts to purify this product were unsuccessful. The remainder of the material consisted of viscous, sticky oils, which slowly solidified into materials with indefinite melting points. No definite crystalline products could be isolated.

Similar results were obtained in several runs using slight variations in the reaction conditions.

Chlorotriphenylsilane and lithium in the presence of methyl phosphate To 0.35 g. (0.05 g. atom) of lithium pieces and 6.1 g. (0.043 mole) of freshly distilled methyl phosphate in a few ml. of THF, there was added 5 ml. of a solution of 6.0 g. (0.02 mole) of chlorotriphenylsilane in

35 ml. of THF. After stirring for a few minutes, a cloudiness was detected, followed by a vigorous evolution of heat. The remaining solution was added over a 30 min. period, without further evidence of reaction. The resulting mixture was stirred for 2 hr. and hydrolyzed in excess dilute acid. Subsequent to the usual work-up and removal of solvents, petroleum ether (b.p. 60-70°) was added to give 4.4 g. (80%) of triphenylsilanol, m.p. 150-153° (mixed m.p.). The mother liquor was chromatographed on alumina. The petroleum ether eluate yielded 0.3 g. (5%) of impure methyltriphenylsilane, m.p. 60-70°. Recrystallization from methanol raised the melting point to 66-68° (mixed m.p.).

Chlorotriphenylsilane and aluminum (attempted)

Run 1 A mixture of 6.0 (0.02 mole) of chlorotriphenylsilane and 1.0 g. (0.04 g. atom) of freshly turned aluminum metal was refluxed in 25 ml. of THF for 5 days. The reaction mixture was hydrolyzed in excess dilute acid. After hydrogen evolution ceased, there remained no insoluble material, i.e., hexaphenyldisilane. Subsequent to the usual work-up, the solvents were removed by distillation and petroleum ether (b.p. 60-70°) was added. The solids were filtered off, and the filtrate chromatographed on an alumina column. Evaporation of the solvent from the petroleum ether eluate left only a trace of material, the infrared spectrum of which did not show the presence of triphenylsilane. The petroleum ether insoluble

material was identified as triphenylsilanol, resulting from hydrolyzed starting material.

Run 2 The same quantities of starting materials and solvent which were used in Run 1, were heated at 140-150° for 18 hr. and at 220-250° for 3 hr. in a steel bomb, agitated by a rocking assembly, under nitrogen pressure (initially 500 p.s.i.g. at room temp.). The work-up and results are identical to those described in Run 1.

1-Bromo-1,1,2,2,3,3,4,4-octaphenyltetrasilane and sodium (attempted) A mixture of 7.3 g. (0.009 mole) of the bromide and 0.23 g. (0.01 g. atom) of sodium was refluxed for 48 hr. in 40 ml. of xylene, which had been dried by storage over sodium and distilled immediately before use. The reaction mixture did not form a purple suspension, as is usual with a normal coupling reaction. Subsequent to hydrolysis of the reaction mixture in excess dilute acid containing crushed ice, filtration gave 0.2 g. (3%) of octaphenylcyclotetrasilane, m.p. 317-320° (mixed m.p.). The filtrate was worked up in the usual manner. Removal of the solvents and the addition of petroleum ether (b.p. 60-70°) gave 0.4 g. of a solid, m.p. 160-170°, the infrared spectrum of which showed the presence of silanol and siloxane groups. The petroleum ether soluble material was chromatographed on alumina and yielded only small amounts of oils in the petroleum ether, cyclohexane, benzene and ether eluates. The methanol fraction gave 3.0 g. of a sticky,

semi-solid material, m.p. 120-150°. The infrared spectra on all of these fractions contained absorption bands characteristic of silanol and/or siloxane groups. Attempts to purify these materials were unsuccessful.

1-Bromo-1,1,2,2,3,3,4,4-octaphenyltetrasilane and magnesium

Run 1 A mixture of 12.1 g. (0.015 mole) of the bromide and 1.0 g. (0.04 g. atom) of magnesium turnings (which had been pretreated with a few drops of ethyl iodide in tetrahydrofuran, and washed free of ethylmagnesium iodide and ethyl iodide with THF until a negative Color Test I⁷⁵ was obtained) was heated together to about 80°. A few ml. of THF was added and after the mixture was brought to reflux, a total of 60 ml. was added in a dropwise fashion over a period of 30 min. After 2.5 hr. of reflux, Color Test I⁷⁵ was positive, with the water layer being a dark blue. The mixture was refluxed overnight, after which Color Test I was negative. The reaction mixture was hydrolyzed in excess dilute acid. The mixture was filtered to give 0.5 g. (4.6%) of impure octaphenylcyclotetrasilane, m.p. 300-315° (cloudy). Recrystallization from benzene gave 0.4 g. (3.8%) of pure material, m.p. 317-320° (mixed m.p.). Subsequent to the usual work-up of the filtrate and removal of solvents, the residue was dissolved in a small amount of benzene and treated with hot petroleum ether (b.p. 60-70°) to give 1.7 g. (15.5%) of impure

Compound (B),⁹⁸ m.p. 400-420° (with sintering at 340°). Recrystallization gave 1.5 g. (13.8%) of pure material, m.p. 445-450° (mixed m.p.). The mother liquor, on standing, deposited 0.4 g. (3.6%) of material, m.p. 155-160° (cloudy). The material resisted attempts at purification. The spectrum indicated it to be impure 1,1,2,2,3,3,4,4-octaphenyltetrasilane. The solvents were removed from the mother liquor, leaving a viscous, brown residue. This was dissolved in hot acetone, treated with decolorizing charcoal, filtered hot, and cooled to give 0.9 g. of a solid, m.p. range 230-290°. The material could not be purified; the infrared spectrum indicated the presence of siloxane groups. The acetone filtrate slowly deposited 1.2 g. (11%) of a solid, m.p. 140-158°. After three recrystallizations from a mixture of benzene and petroleum ether (b.p. 60-70°), 0.5 g. (4.5%) of pure 1,1,2,2,3,3,4,4-octaphenyltetrasilane was isolated, m.p. 160-162° (mixed m.p.). Concentration of the acetone solution gave 0.6 g. (5.5%) of a solid, m.p. range 110-140°. Attempts to purify this material were not successful. The infrared spectrum indicated that it might be impure 1,1,2,2,3,3,4,4,5,5-decaphenylpentasilane.¹⁰⁵ No other crystalline products could be isolated; the infrared spectrum on the residue obtained

¹⁰⁵This material was proposed to be a decasilane.⁹⁴ However, more recent evidence indicates that it is a pentasilane.⁸²

from the acetone solution indicated the presence of siloxane groups.

Run 2 An attempt to initiate the reaction between the same amount of bromide used in Run 1 and untreated magnesium by refluxing the THF for 2 hr. resulted in no evidence of a reaction. The addition of a few pieces of magnesium which had been pretreated with iodine, followed by refluxing for another 2 hr., did not appear to effect initiation. A few turnings of magnesium, pretreated with ethyl iodide as in Run 1, were added; refluxing for 2 hr. caused the mixture to become cloudy. The mixture was refluxed an additional 22 hr., decanted through a loose glass-wool plug, and filtered. The solids were washed with benzene, dilute acid, and distilled water to give, after drying, 0.9 g. (8.2%) of octaphenylcyclotetrasilane, m.p. 318-320° (mixed m.p.). The solvent was removed from the filtrate, benzene added, and the mixture filtered to give an additional 0.3 g. (2.7%) of octaphenylcyclotetrasilane, m.p. 317-322° (mixed m.p.). Concentration of the filtrate and addition of hot petroleum ether (b.p. 60-70°) gave 1.5 g. (13.7%) of Compound (B), m.p. 460-465° (mixed m.p.). No attempt was made to isolate products from the sticky, semi-solid residue obtained by evaporation of the solvents from the mother liquor. The infrared spectrum contained strong absorption bands characteristic of SiOH and SiOSi groups, and a band of medium intensity due to SiH bonds.

Run 3 The reaction was carried out as described in Run 1. A negative Color Test I⁷⁹ was obtained after one hour of reflux, but was positive after an additional 15 min. reflux period, with the water layer being blue. A Color Test I taken after another 30 min. of refluxing was positive, but appeared to be weaker. The reaction mixture was decanted away from the magnesium and added to 2.1 g. (0.015 mole) of trimethyl phosphate in 10 ml. of THF. Color Test I was negative after completion of the addition. The mixture was allowed to stand overnight and was filtered. The solids were washed with benzene, dilute acid, and distilled water to give, after drying, 0.7 g. (6.4%) of octaphenylcyclotetrasilane, m.p. 317-320° (mixed m.p.). The filtrate was hydrolyzed in dilute acid and worked up in the usual manner. Removal of the solvent, dissolution of the residue in a small amount of benzene, and addition of hot petroleum ether (b.p. 60-70°) gave 3.0 g. (27.2%) of solid, m.p. 150-160°. Recrystallization gave 2.4 g. (22%) of 1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. 160-162° (mixed m.p.). No further pure products were isolated.

Run 4 The reaction was carried out as described in Run 3. A negative Color Test I was obtained after 1 hr. of refluxing, but was positive after an additional 15 min. of heating. The mixture was allowed to cool for 15 min., decanted through a loose glass-wool plug, and added

to excess trimethyl phosphate. Color Test I was negative immediately after the addition. The mixture was hydrolyzed in excess dilute acid, and filtered to give 0.65 g. (5.9%) of octaphenylcyclotetrasilane, m.p. 319-322° (mixed m.p.). Subsequent to the usual work-up of the filtrate, the solvents were removed and benzene added. The mixture was filtered to give an additional 0.6 g. (5.5%) of octaphenylcyclotetrasilane, m.p. 318-320° (mixed m.p.). The benzene filtrate was concentrated and hot petroleum ether was added to give an oil. Removal of the solvents and crystallization from ethyl acetate yielded 0.3 g. (2.7%) of Compound (B), m.p. 452-456° (mixed m.p.). Upon standing, the filtrate gave 1.9 g. (17.3%) of a solid, m.p. 115-125°. Fractional recrystallization from ethyl acetate gave 0.7 g. (6.4%) of 1,1,2,2,3,3,4,4,5,5-decaphenylpentasilane,¹⁰⁵ m.p. 145-147°, (mixed m.p.).¹⁰⁶

5-Chloro-5-methyldibenzosilole¹⁰⁷ and magnesium A few ml. of a solution of 4.0 g. (0.02 mole) of 5-chloro-5-methyldibenzosilole was added to a suspension of 10 ml. of THF and 4.8 g. (0.02 g. atom) of 40 mesh magnesium, which had been pretreated with a couple drops of ethyl iodide, and

¹⁰⁶H. Gilman and D. J. Peterson, Chemistry Department, Iowa State University of Science and Technology, Ames, Iowa. Compound obtained from hydrolysis of the dilithio reagent resulting from cleavage of Compound (B)⁹⁸ with lithium, private communication, 1961.

¹⁰⁷H. Gilman and R. D. Gorsich, J. Am. Chem. Soc., 80, 1883 (1958).

rinsed free of Grignard reagent and ethyl iodide by successive washings with THF. This mixture was heated at reflux for 30 min., when a cloudiness was detected. The remainder of the solution of chloride was added in a dropwise fashion over a period of 2 hr., while the reaction mixture was maintained at reflux. Color Test I was negative during the addition, upon completion of the addition, after 1 hr. reflux, and after 12 hr. of reflux. The mixture was refluxed for 24 hr. with the solvent escaping overnight. Fifty ml. of THF was added and the mixture refluxed for an additional 4 hr. Color Test I was still negative. The mixture was decanted from the magnesium and hydrolyzed in excess dilute acid. Subsequent to the usual work-up and removal of the solvents, the residue was crystallized from ethanol to give 3.0 g. (88.3%) of 5,5'-dimethyl-5,5'-bi-(di-benzosilole),¹⁰⁸ m.p. 180-182° (mixed m.p.). An infrared spectrum on the residue obtained by removal of the solvent from the mother liquor showed absorption bands characteristic of silanol and siloxane groups; there was no evidence for material containing the silicon-hydrogen group.

1-Chloro-1,1,2,2-tetraphenyldisilane and magnesium A mixture of 6.0 g. (0.015 mole) of 1-chloro-1,1,2,2-tetraphenyldisilane and 1.2 g. (0.05 g. atom) of magnesium (which had been pretreated with ethyl iodide and washed thoroughly

¹⁰⁸Ibid., 3243 (1958).

with THF) was refluxed in 50 ml. of THF for 24 hr. Color Test I was negative after 3 hr. of reflux and also after 24 hr. The magnesium was removed by decantation, and the reaction mixture hydrolyzed in excess dilute acid. Subsequent to the usual work-up and removal of solvent, the residue was crystallized from a small amount of benzene and petroleum ether (b.p. 60-70°) to give 2.8 g. (51%) of impure 1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. 150-160°. Recrystallization gave 2.0 g. (36.5%) of pure material, m.p. 160-162° (mixed m.p.).

Triphenylsilyllithium and Aluminum Chloride

Triphenylsilyllithium, prepared in THF by lithium cleavage of 5.2 g. (0.01 mole) of hexaphenyldisilane, was added to a solution of 0.89 g. (0.0067 mole) of freshly sublimed aluminum chloride. The brown color of the silyllithium solution rapidly gave way to a light pink solution. A negative Color Test I was obtained after the addition. A portion of the solution was removed and hydrolyzed in excess deuteriochloric acid. While this was being worked up, 7.3 g. (0.01 mole) of octaphenylcyclotetrasilane was added to the main body of the reaction mixture, which was subsequently refluxed for 4 days. The infrared spectrum of the triphenylsilane obtained from that portion of the mixture which was hydrolyzed in deuteriochloric acid showed only a very weak absorption band due to the silicon-deuterium group.

Work-up of the main body of the reaction mixture subsequent to acid hydrolysis, gave 6.9 g. (94.5%) of recovered octaphenylcyclotetrasilane, m.p. 319-322° (mixed m.p.); and 1.0 g. (20%) of triphenylsilane, b.p. 151-153° (0.55 mm.), m.p. 42-44°, (mixed m.p.). No pure products were obtained upon chromatographing the distillation residue on an alumina column. However, infrared spectra on some of the various fractions contained strong absorption bands characteristic of aliphatic carbon-hydrogens, indicative of reaction with solvent.

Pyrolysis Reactions

Octaphenylcyclotetrasilane

Five grams (0.007 mole) of octaphenylcyclotetrasilane was placed in a dry ampoule of ca. 20 ml. volume. The tube was flushed five times with dry, oxygen-free nitrogen by alternately evacuating and refilling. The sample was sealed under ca. 3 mm. of nitrogen pressure, heated in an oven at $360 \pm 10^\circ$ for 3 hr., and cooled. Only slight yellowing of the material had occurred. The ampoule was opened and the residue washed out with hot benzene. Upon cooling, the solids were filtered to give 2.4 g. (48%) of recovered starting material, m.p. 318-322° (mixed m.p.). Attempts to crystallize the benzene soluble portion yielded only small amounts of solids, m.p. range 190-240°. The infrared spectra of these fractions indicated the presence of silicon-hydrogen

groups. The mother liquor gave, on evaporation of solvent, a sticky, polymeric-like residue.

Compound (B)

Run 1 The reaction was carried out as described in the preceding paragraph. Five grams of Compound (B) was heated for a few minutes at 450° to melt the sample and then heated at $350 \pm 10^{\circ}$ for 9 hr. Upon cooling, the residue was dissolved in a small amount of benzene and treated with hot petroleum ether (b.p. $60-70^{\circ}$) to give 4.7 g. (94%) of recovered starting material, m.p. $460-462^{\circ}$ (mixed m.p.). Attempts to crystallize the sticky residue obtained by evaporation of the solvents from the mother liquor were unsuccessful.

Run 2 The reaction was carried out as described in preceding experiments, except that the ampoule used was modified with a side-arm receiver, which was cooled in a slurry of Dry Ice and acetone during the run. Five grams was heated at $410 \pm 10^{\circ}$ for 4 hr. A yellow, polymeric-like residue, 4.3 g. (86%) was obtained and could not be crystallized. The distillate contained silicon-hydrogen groups, as indicated by its infrared spectrum. It was distilled under reduced pressure to give ca. 0.1 g. of impure diphenylsilane, b.p. approximately 70° (3.0 mm.), n_D^{20} 1.5780 (identified by its infrared spectrum); and 0.2 g. of material, b.p. $105-110^{\circ}$ (0.05 mm.), the spectrum

of which indicated this material to be 1,1,2,2-tetraphenyl-disilane. Attempts to purify this material were unsuccessful.

Preparation of Organosilicon Chlorides

from the Corresponding Hydrides

Triphenylsilane and mercuric chloride

In ether A suspension of 5.2 g. (0.02 mole) of triphenylsilane and 10.8 g. (0.04 mole) of mercuric chloride in 50 ml. of diethyl ether was stirred for 24 hr., while the vessel was being swept with oxygen-free, dry nitrogen. The ether slowly evaporated and was replenished as needed. Petroleum ether (b.p. 60-70°) was added and the ether removed by distillation. The suspension was filtered hot to remove mercury salts. Upon concentration and cooling, there was obtained 2.9 g. (49.5%) of impure chlorotriphenylsilane, m.p. 86-92°. Recrystallization afforded 2.2 g. (40%) of pure product, m.p. 95-96° (mixed m.p.).

In benzene The reaction was carried out as described in the preceding experiment, except 50 ml. of benzene was used as solvent. After 24 hr. of stirring at room temperature, petroleum ether (b.p. 77-115°) was added and the benzene removed by distillation. The suspension was filtered hot to remove the mercury salts. From the filtrate, upon concentrating and cooling, there was obtained 2.1 g. (36%) of impure chlorotriphenylsilane, m.p. 90-95°. Recrystallization from petroleum ether (b.p. 60-70°) afforded 1.9 g.

(30%) of pure material, m.p. 95-96° (mixed m.p.).

In THF The reaction was carried out as described in the preceding experiments with THF as solvent. Subsequent to 24 hr. of stirring, only a small amount of solvent remained, which was removed under reduced pressure. Petroleum ether (b.p. 60-70°) was added and the hot suspension filtered. Concentration and cooling gave 4.8 g. (82%) of crude product, m.p. 87-92°. Recrystallization gave 4.2 g. (72%) of pure chlorotriphenylsilane, m.p. 95-96° (mixed m.p.).

1,1,2,2-Tetraphenyldisilane and mercuric chloride

A mixture of 18.33 g. (0.05 mole) of 1,1,2,2-tetraphenyldisilane and 27.1 g. (0.1 mole) of mercuric chloride was stirred in 100 ml. of ether at room temperature for 18 hr. All of the solvent had evaporated. Petroleum ether (b.p. 28-38°) was added and the salts removed by filtration. The solvent was removed from the filtrate and the oily residue distilled under reduced pressure to give 1.0 g. of forerun, b.p. 165-183° (0.003 mm.) and 9.8 g. (49%) of 1-chloro-1,1,2,2-tetraphenyldisilane, b.p. 183-187° (0.003 mm.), m.p. 45-50°.

Anal. calcd. for $C_{24}H_{21}ClSi_2$: Si, 14.16. Found: Si, 14.16, 14.21.

The melting point was raised to 47-50° upon recrystallization from dry t-amyl alcohol.

A similar yield was obtained when the reaction was run using THF as solvent.

Derivatization with methyllithium To a solution of 4.0 g. (0.01 mole) of 1-chloro-1,1,2,2-tetraphenyl-disilane in 20 ml. of ether, there was added 0.01 mole of methyllithium in 10 ml. of ether. Color Test I was negative within a few min. after completion of the addition. The mixture was hydrolyzed in dilute acid and worked up in the usual manner. Removal of the solvents and crystallization from ethanol yielded 3.2 g. (85.2%) of 1-methyl-1,1,2,2-tetraphenyldisilane, m.p. 64-66°. Recrystallization from a small amount of petroleum ether (b.p. 60-70°) did not alter the melting point. A mixed melting point with a sample prepared in poor yield from the reaction between methyldi-phenylsilyllithium and chlorodiphenylsilane was undepressed. Also, a mixed melting point with a sample obtained from the reaction between octaphenylcyclotetra-silane and methyllithium was undepressed.⁸⁹

Anal. calcd. for $C_{25}H_{24}Si_2$: Si, 14.92. Found: Si, 14.95, 14.80.

1,1,2,2,3,3,4,4-Octaphenyltetrasilane and mercuric chloride

A mixture of 2.0 g. (0.0027 mole) of 1,1,2,2,3,3,4,4-octaphenyltetrasilane and 3.0 g. (0.011 mole) of mercuric chloride was stirred for 24 hr. in THF. The solvent had completely evaporated in the stream of dry nitrogen. The residue was refluxed in benzene for 1 hr. and filtered. The benzene was removed and the residue crystallized from ether to give 2.0 g. of solid, m.p. 150-180°. Attempts to purify this material were unsuccessful. Infrared analysis on the various fractions obtained showed the presence of silicon-hydrogen groups.

1,2-Dimethyl-1,2-diphenyldisilane

Chlorine Chlorine gas was passed slowly through a carbon tetrachloride solution of 47.7 g. (0.2 mole) of 1,2-dimethyl-1,2-diphenyldisilane until a slight yellow coloration remained. The excess chlorine was removed in a stream of dry nitrogen. The solvent was removed and the residue distilled under reduced pressure to give 38.4 g. of material, b.p. 35-55° (0.015 mm.). The low boiling point of this material indicated that silicon-silicon bond cleavage had occurred, and it was not investigated further. The distillation was continued but gave only small amounts of materials boiling in the range 130-170° (0.006 mm.). No attempt was made to purify these fractions.

Mercuric chloride To 24.2 g. (0.1 mole) of the disilane dissolved in 100 ml. of benzene, there was added a

solution of 54.3 g. (0.2 mole) of mercuric chloride in 50 ml. of THF. The reaction mixture was stirred at room temperature for 24 hr. No further evolution of hydrogen chloride was evident. The solvents were removed by distillation and the residue treated with petroleum ether (b.p. 60-70°). The salts were removed by filtration, the solvent distilled from the filtrate and the remaining residue distilled under reduced pressure to give several fractions of dark yellow oils: 9.4 g., b.p. 94-105° (0.006 mm.); 5.3 g., b.p. 100-105° (0.005 mm.); and 1.1 g., b.p. 120-130° (0.003 mm.). No attempt was made to purify these fractions.

Reaction of Hexachlorodisilane with
Tetramethylenedimagnesium Bromide

1:1 Mole ratio, followed by reduction with lithium aluminum hydride

To 49.2 g. (0.183 mole) of hexachlorodisilane in 500 ml. of ether, there was added slowly 0.183 mole of tetramethylenedimagnesium bromide in 150 ml. of ether. The ether and any unreacted hexachlorodisilane were removed by distillation from petroleum ether (b.p. 60-70°). The magnesium salts were removed by filtration under nitrogen. The salts were washed with petroleum ether and benzene, and the washings combined with the filtrate. These solvents were removed by distillation and replaced with ether. The resulting solution was added to 7.6 g. (0.2 mole) of lithium aluminum hydride suspended in 100 ml. of ether. Subsequent to completion of

the addition, the mixture was refluxed for 4 hr. and hydrolyzed in crushed ice containing excess acid. After the usual work-up and removal of solvents, the residue was distilled under reduced pressure to give a large number of fractions, none of which were constant boiling; the boiling points ranged from 45-135° (105 mm.) to 65-113° (2 mm.). During the distillation, the vapors ignited. The products were not investigated further.

1:2 Mole ratio, followed by reduction with lithium aluminum hydride

The Grignard reagent, 0.54 mole in 388 ml. of ether, was added slowly to 72.1 g. (0.27 mole) of hexachlorodisilane dissolved in a mixture of 300 ml. of ether and 100 ml. of petroleum ether (b.p. 60-70°). After stirring for 1 hr., 6.0 g. (0.15 mole) of solid lithium aluminum hydride was added slowly. The resulting mixture was stirred for 12 hr. at room temperature and refluxed for 3 hr. Subsequent to hydrolysis as described in the preceding experiment, and the usual work-up, the solvents were removed and the residue distilled under reduced pressure to give 1.0 g. of forerun, b.p. 56-85° (12 mm.), and 22.1 g. (52.4%) of an oil, b.p. 90-94° (12 mm.). This material was not further purified when it was shown to be primarily bis-(cyclo-tetramethylene)-disilane by derivatization with phenyl-lithium as described in the following paragraph.

To 5.1 g. (0.03 mole) of the crude bis-(cyclotetramethylene)-disilane, there was added 0.07 mole of phenyllithium in 50 ml. of ether. Subsequent to hydrolysis in dilute acid and the usual work-up, the solvents were removed and the residue distilled under reduced pressure to give 8.4 g. (89.4%) of slightly impure bis-(cyclotetramethylene-phenyl)-disilane, b.p. 142-155° (0.01-0.015 mm.), m.p. 42-46°. Recrystallization from petroleum ether (b.p. 60-70°) raised the melting point to 44-47° (mixed m.p.)¹⁰⁹

Reactions Involving Aluminum Chloride as Catalyst In THF (attempted)

Solutions of aluminum chloride in THF were prepared by slowly adding the solvent to the anhydrous salt, cooled to -20°. A violent reaction occurred when the reagents were mixed at room temperature, causing the solution to turn a purplish color.

Benzyl chloride and benzene To 10 g. (0.08 mole) of benzyl chloride and 50 ml. of benzene, there was added 4.0 g. (0.03 mole) of aluminum chloride dissolved in 90 ml. of THF. The reaction mixture was stirred for 12 hr. at room temperature and refluxed for 24 hr. There was no

¹⁰⁹H. Gilman and G. D. Lichtenwalter, Chemistry Department, Iowa State University of Science and Technology, Ames, Iowa. Product obtained during studies on cyclic organosilicon compounds, private communication, 1959. This material was originally obtained as an oil. However, it had solidified on standing, m.p. 44-47°.

evidence of a reaction. The mixture was hydrolyzed in water and worked up in the usual manner. After removing the ether, a mixture of benzene and benzyl chloride was distilled and collected over the range 80-144°. An attempted reduced-pressure distillation of the small amount of material remaining in the distillation residue afforded no diphenylmethane.

Benzoyl chloride and benzene To 33.0 g. (0.25 mole) of aluminum chloride dissolved in 185 ml. of THF, there was added 14.0 g. (0.1 mole) of benzoyl chloride dissolved in 50 ml. of benzene. The mixture was stirred for 12 hr. at room temperature, refluxed for 40 hr., and hydrolyzed in crushed ice. A precipitate formed and was removed by filtration. This material, presumably aluminum benzoate, was heated in a mixture of benzene and 5% hydrochloric acid. Subsequent to the usual work-up and removal of solvent, there was obtained 9.5 g. (78%) of benzoic acid, m.p. 120-122° (mixed m.p.). The filtrate was worked up in the usual manner. The solvents were removed by distillation to leave a small amount of residue, the infrared spectrum of which showed no carbonyl band, indicating the absence of benzophenone.

Hexaphenyldisilane A mixture of 2.7 g. (0.02 mole) of aluminum chloride and 10.2 g. (0.02 mole) of hexaphenyldisilane was refluxed in 75 ml. of THF for 52 hr. The reaction mixture was poured into water, the solids filtered

off, washed with water, ethanol, and ether to give 10.1 g. (99.2%) of recovered hexaphenyldisilane, m.p. 362-365° (mixed m.p.).

Compound (B)⁹⁸ A mixture of 10.9 g. of Compound (B) and 1.4 g. (0.01 mole) of aluminum chloride was stirred at room temperature in 75 ml. of THF for 48 hr. The reaction mixture was hydrolyzed in water and worked up in the usual manner. Subsequent to removal of solvents, there was recovered 10.5 g. (96%) of starting material, m.p. 447-455° (mixed m.p.).

Hexaphenyldisilane in benzene

A mixture of 10.2 g. (0.02 mole) of hexaphenyldisilane and 2.7 g. (0.02 mole) of aluminum chloride was refluxed in 50 ml. of benzene for 20 hr. The reaction mixture was hydrolyzed in water and filtered. The solids were washed with water, ethanol, ether, and benzene to give 6.8 g. (66.7%) of recovered starting material, m.p. 362-365° (mixed m.p.). No crystalline products could be isolated from the benzene soluble fraction.

Compound (B)⁹⁸ in nitrobenzene

A mixture of 10.9 g. of Compound (B) and 1.4 g. (0.01 mole) of aluminum chloride was stirred for 16 hr. at room temperature in 50 ml. of nitrobenzene. The black mixture was hydrolyzed in dilute acid. A black, gummy, semi-solid material was obtained which did not dissolve in cold benzene.

It was extracted with the same solvent and not investigated further. The benzene extract was combined with the filtrate and, subsequent to the usual work-up and removal of solvents under reduced pressure, the remaining residue was crystallized from a mixture of benzene and petroleum ether (b.p. 60-70°) to give 1.6 g. (14.7%) of recovered starting material, m.p. 450-455° (mixed m.p.). No other crystalline materials could be isolated from the mother liquor.

Reactions Involving Wittig Reagents

Methylenetriphenylphosphorane

Methylenetriphenylphosphorane was prepared in ether from methyltriphenylphosphonium bromide and phenyllithium.⁹⁵ The only difference between the published procedure and the one used herein was that the phenyllithium was prepared from the reaction between bromobenzene and lithium instead of from diphenylmercury and lithium.⁹⁵

Octaphenylcyclotetrasilane Methylenetriphenylphosphorane, prepared from 2.5 g. (0.007 mole) of methyltriphenylphosphonium bromide and 0.007 mole of phenyllithium in a total of 40 ml. of ether, and 5.0 g. (0.007 mole) of octaphenylcyclotetrasilane were refluxed for 3 hr. in a THF suspension after removal of the ether. The light yellow suspension, which gave a negative Color Test I,⁷⁵ was hydrolyzed in dilute acetic acid. The sticky solid obtained was washed with methanol and dried to give 3.0 g. (60%) of

recovered octaphenylcyclotetrasilane, m.p. 317-320° (mixed m.p.). The methanol used to wash the solids was evaporated to give a brown oil. Treatment with ethyl acetate gave 0.5 g. (25%) of methyltriphenylphosphonium bromide, m.p. 225-230° (mixed m.p.). The aqueous layer, on standing, turned cloudy. It was extracted with ether and filtered to give 0.3 g. of unidentified material, m.p. 110-140°. Recrystallizations failed to give any pure products. The infrared spectrum showed the presence of bands characteristic of phenyl-silicon, silicon-hydrogen, silanol, and siloxane groups. The ether extracts were worked up in the usual manner. Subsequent to the removal of the solvents, a sticky solid was obtained. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60-70°) gave 0.5 g. (9.5%) of impure 1,1,2,2,3,3,4,4-octaphenyltetrasilan-1-ol, m.p. 156-162°. Recrystallization raised the melting point to 180-182° (mixed m.p.).

A second run was carried out using the same quantities of starting materials. After refluxing the THF suspension for 2 hr., 1.3 g. (0.007 mole) of benzophenone was added, and the mixture refluxed an additional 2 hr. Work-up in a manner similar to that described in the preceding paragraph gave 1.0 g. (20%) of recovered octaphenylcyclotetrasilane, m.p. 316-320° (mixed m.p.); 1.4 g. (57%) of methyltriphenylphosphonium bromide, m.p. 227-229° (mixed m.p.); 0.5 g. (10%) of impure, m.p. 145-164°, and 0.3 g. (6%) of

pure 1,1,2,2,3,3,4,4-octaphenyltetrasilane-1-ol, m.p. 182-184° (mixed m.p.); and 1.4 g. (28%) of material, m.p. 110-125°, from which there was obtained, after four recrystallizations from ethyl acetate, 0.3 g. (6%) of the same siloxane obtained upon hydrolysis of 1-bromo-1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. 140-142° (mixed m.p.).¹¹⁰

Chlorotrimethylsilane, followed successively by phenyllithium and benzophenone

Run 1 To an ether suspension of methylenetriphenylphosphorane, prepared from 7.1 g. (0.02 mole) of methyltriphenylphosphonium bromide and 0.02 mole of phenyllithium in a total of ca. 50 ml. of ether, there was added 2.2 g. (0.02 mole) of chlorotrimethylsilane in 50 ml. of ether solution. There was an immediate formation of a light yellow precipitate. The reaction mixture was allowed to stir for 2 hr. at room temperature, followed by the addition of 0.02 mole of phenyllithium. After stirring the resulting mixture for 2 hr., a Color Test I⁷⁵ was weakly positive. Benzophenone, 3.6 g. (0.02 mole), was added directly to the dark suspension along with 50 ml. of THF. The ether was removed by distillation and the remaining suspension refluxed for 24 hr. The reaction mixture was hydrolyzed in dilute acid

¹¹⁰H. Gilman and G. Chainani, Chemistry Department, Iowa State University of Science and Technology, Ames, Iowa. Data from polysilane studies, private communication, 1961. NMR study indicates that the material is not the expected symmetrical siloxane.

and worked up in the usual manner. Subsequent to the removal of solvents, petroleum ether (b.p. 60-70°) was added to give 3.6 g. (64.9%) of triphenylphosphine oxide, m.p. 155-156° (mixed m.p.). The petroleum ether was removed from the mother liquor and the addition of ethanol gave 0.7 g. (19.4%) of impure tetraphenylallene, m.p. 155-160°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60-70°) raised the melting point to 164-165° (mixed m.p. with an authentic sample, prepared by the pyrolysis of barium diphenylacetate according to published directions¹¹¹). The solvent was removed from the mother liquor and the residue distilled under reduced pressure to give several fractions: 0.1 g., b.p. 50-55° (60 mm.), the infrared spectrum of which indicated it to be impure trimethylphenylsilane; 0.1 g., b.p. 100-105° (1.7 mm.); 1.0 g., b.p. 105-110° (1.7 mm.), n_D^{20} 1.5921. The infrared spectra of the last two fractions were similar to that of 1,1-diphenylethylene except for weak absorption bands usually associated with the trimethylsilyl group. These materials were combined and redistilled to give several small fractions boiling in the range 88-102° (1.5 mm). An analysis on one of the fractions, b.p. 100-102° (1.5 mm.), gave the combined carbon and hydrogen content as 97.5%, a value too high for (2,2-diphenylvinyl)trimethylsilane, which requires 88.7%. An additional 0.3 g. (5%)

¹¹¹D. Vorländer and C. Siebert, Ber., 39, 1024 (1906).

of triphenylphosphine oxide was isolated from the initial distillation residue, m.p. 155-157° (mixed m.p.).

Run 2 In a manner similar to that described in Run 1, methylenetriphenylphosphorane, prepared from 14.2 g. (0.04 mole) of methyltriphenylphosphonium bromide and 0.04 mole of phenyllithium in ether, was allowed to react with 4.3 g. (0.04 mole) of chlorotrimethylsilane. To the resulting suspension, another 0.05 mole of phenyllithium was added. The reaction mixture was stirred at room temperature for 2 hr. and refluxed for 30 min.; 50 ml. of THF was added, and the mixture refluxed for 1 hr., during which most of the ether was removed. A negative Color Test I⁷⁵ was obtained. The dark mixture was cooled, 7.3 g. (0.04 mole) of benzophenone added along with another 50 ml. of THF, and the resulting solution refluxed for 24 hr. During this time, most of the solvent had escaped, leaving a brown paste. Ether was added and the mixture worked up as described in Run 1. Subsequent to removal of the solvents, acetone was added to the residue and the insoluble material filtered to give 1.4 g. (21%) of impure tetraphenylallene, m.p. 160-163°. Recrystallization from acetone, after treatment with decolorizing charcoal, gave 1.2 g. (17.5%) of pure product, m.p. 164-166° (mixed m.p.). Upon concentration of the mother liquor, there was obtained an additional 1.0 g. (14.5%) of impure tetraphenylallene, m.p. 156-159°. Recrystallization with charcoaling gave 0.7 g. (10.1%) of

pure material, m.p. 164-165° (mixed m.p.). The total yield of tetraphenylallene was 34.5% crude and 27.6% pure. The solvents were removed from the mother liquor and the residue distilled under reduced pressure to give several fractions: 0.2 g., b.p. 50-84° (1.4 mm.); 0.6 g., b.p. 85-90° (1.4 mm.); 0.3 g., b.p. 50-74° (0.25 mm.); 0.3 g., b.p. 95-103° (0.25 mm.); and 0.5 g., b.p. 103-118° (0.25 mm.). The infrared spectra of these fractions indicated them to be complex mixtures. They were not investigated further. From the distillation residue, there was isolated 1.0 g. (9.1%) of triphenylphosphine oxide, m.p. 156-157° (mixed m.p.).

Run 3 The reaction was carried out as described in Run 1, except that xylene was added instead of THF, and two molar equivalents of benzophenone was used. The final mixture, after removal of the ether, was refluxed for 70 hr. Subsequent to hydrolysis, work-up, removal of solvent, and addition of petroleum ether (b.p. 60-70°), there was obtained 2.3 g. (41.5%) of impure triphenylphosphine oxide, m.p. 140-150°. Recrystallization raised the melting point to 155-157° (mixed m.p.). Removal of the solvent from the mother liquor and treatment with a small amount of acetone afforded no tetraphenylallene. Distillation, after removing the solvent, gave four fractions of material, boiling between 90-112° (1.7 mm.). The infrared spectra of these materials indicated them to be mixtures of 1,1-diphenylethylene and benzophenone. One of the fractions partially solidified and was filtered.

The solid was identified as benzophenone, m.p. 44-46° (mixed m.p.). The distillates were not investigated further.

Chlorotrimethylsilane, followed successively by phenyllithium and Michler's ketone (attempted) The reaction was carried out in an analogous manner to that described in the preceding experiment, Run 1, except that Michler's ketone, 5.4 g. (0.02 mole) was used. Subsequent to the removal of the ether, the THF suspension was refluxed for 18 hr. The dark green mixture was hydrolyzed in excess dilute hydrochloric acid. The colored aqueous layer was washed with ether and neutralized by the addition of sodium carbonate. The solids formed were washed with water and dried to give 4.4 g. (81.5%) of recovered, impure Michler's ketone, m.p. 158-164°. Recrystallization raised the melting point to 164-166° (mixed m.p.). The organic layer was worked up in the usual manner, the solvents removed, and petroleum ether added to give 1.0 g. (18%) of triphenylphosphine oxide, m.p. 154-155° (mixed m.p.). Removal of the solvent from the mother liquor and distillation under reduced pressure gave 0.2 g. of impure hexamethyldisiloxane, b.p. 55-75° (40 mm.), identified by its infrared spectrum. Further attempts to distill at a lower pressure gave only traces of material. Treatment of the black distillation residue with a small amount of acetone gave no insoluble material.

Chlorotriphenylsilane, followed successively by phenyl-
lithium and benzophenone Methylenetriphenylphosphorane was prepared from 7.2 g. (0.02 mole) of methyltriphenylphosphonium bromide and 0.02 mole of phenyllithium in a total of 75 ml. of ether. Addition of 6.0 g. (0.02 mole) of chlorotriphenylsilane resulted in an immediate formation of a light yellow precipitate. The reaction mixture was allowed to stir at room temperature for 2 hr. A second equivalent of phenyllithium was added, and after stirring for 2 hr., Color Test I⁷⁵ was negative; 3.6 g. (0.02 mole) of benzophenone and 50 ml. of THF were added. The ether was removed by distillation and the THF suspension refluxed for 3 hr. The brown, homogeneous mixture was hydrolyzed in dilute hydrochloric acid. An oily interphase formed, which was separated with the aqueous layer. The oily material solidified on standing. It was filtered, treated with hot benzene, and refiltered. The material was boiled with hot water, filtered, and dried to give 1.6 g. (30%) of impure hexaphenyldisiloxane, m.p. 212-220°. Recrystallization raised the melting point to 224-226° (mixed m.p.). An additional 1.5 g. (28.2%) of hexaphenyldisiloxane, m.p. 224-226° (mixed m.p.) was obtained upon cooling the benzene filtrate. The wash water and the aqueous layer were combined and evaporated under a jet of air, leaving a gummy residue. The material was taken up in chloroform, dried over sodium sulfate, and precipitated by the addition of benzene to give

3.8 g. (51.6%) of impure methyltriphenylphosphonium salts, m.p. 220-230°. Its spectrum was superimposable upon that of the pure bromide. The organic layer was worked up in the usual manner and, subsequent to the removal of solvent, a light brown oil was obtained. Treatment with cold methanol left 0.4 g. (6%) of impure tetraphenylsilane, m.p. 200-220°. Recrystallization from ethyl acetate raised the melting point to 230-232° (mixed m.p.). The methanol filtrate was evaporated and yielded a brown oil, which was dissolved in benzene. The solution was treated with decolorizing charcoal, filtered and concentrated. The addition of hot petroleum ether (b.p. 60-70°) and cooling gave 1.5 g. of solid material, m.p. 120-130°. Recrystallization, after treatment with decolorizing charcoal, gave 1.1 g. of crystals, m.p. 122-123°. The melting point remained constant on subsequent recrystallization. This material was identified as a 1:1 mole-ratio complex of triphenylsilanol and triphenylphosphine oxide in the following manner. The infrared spectrum indicated the presence of a hydroxyl group. An NMR spectrum showed, in addition to the hydroxylic proton, only aromatic hydrogens; upon integration, the ratio of aromatic to hydroxylic protons was 29:1, indicating six phenyl groups for each hydroxyl group. A molecular weight determination in camphor by the Rast method gave inconsistent values ranging from 300-430. Silicon analyses were carried out in the usual manner; the

residues were fused with sodium carbonate, and the silica reprecipitated after dehydration from hydrochloric acid. The filtrate was concentrated and gave a positive qualitative test for phosphorus with ammonium molybdate. The remainder of the structure determination was based on the following analytical data.

Anal. calcd. for $C_{36}H_{31}O_2PSi$: C, 77.97; H, 5.65; Si, 5.06. Found: C, 77.94, 78.01; H, 5.66, 5.80; Si, 5.06, 4.70.

This complex was also obtained simply by crystallization of a prepared mixture of 1.0 g. (0.003 mole) of triphenylphosphine oxide (m.p. 156-157°), and 1.0 g. (0.003 mole) of triphenylsilanol (m.p. 154-155°), from a mixture of benzene and petroleum ether (b.p. 60-70°); 1.8 g. (90%) of crystals were obtained which melted at 123-124° and did not depress the melting point of the material isolated from the reaction mixture. The infrared spectra were superimposable.

The solvents were removed from the original mother liquor and the residue chromatographed on alumina. The petroleum ether (b.p. 60-70°), cyclohexane, and benzene eluates, upon removal of the solvents, gave oils, the infrared spectrum of which indicated that they were mainly benzophenone. Attempts to crystallize these oils were unsuccessful. From the methanol eluate, there was obtained 0.7 g. (12.5%) of impure triphenylsilanol, m.p. 140-150°.

Recrystallization raised the melting point to 152-155° (mixed m.p.).

Similar results were obtained from two other runs. In one case, the final THF suspension was refluxed for 24 hr. prior to hydrolysis. The other run was carried out using xylene in the place of THF; the mixture was refluxed for 64 hr. after removal of the ether.

Chlorotriphenylsilane, followed successively with phenyllithium and Michler's ketone (attempted) The reaction was carried out as described in the preceding experiment, with the exception that 5.4 g. (0.02 mole) of Michler's ketone was added instead of benzophenone and the reaction mixture, subsequent to removal of the ether, was refluxed for 18 hr. Hydrolysis in excess dilute acid afforded an oil which solidified and was filtered off. Recrystallization from ethyl acetate gave 5.0 g. (69.5%) of impure methyltriphenylphosphonium salt, m.p. 200-230° (identified by its infrared spectrum). The aqueous layer was neutralized by the addition of sodium carbonate and yielded 4.1 g. (76%) of recovered ketone, m.p. 173-175° (mixed m.p.). Work-up of the organic layer afforded 4.4 g. (78%) of impure triphenylsilanol, m.p. 135-144°. Recrystallization raised the melting point to 152-154° (mixed m.p.).

(2,2-Diphenylvinylidene)triphenylphosphorane

Preparation of (2,2-diphenylvinyl)triphenylphosphonium bromide The method used was similar to that described for the preparation of tetraphenylphosphonium bromide.¹¹² 2,2-Diphenylvinylmagnesium bromide was prepared from 3.0 g. (0.12 mole) of 2,2-diphenylvinyl bromide¹¹³ and 4.9 g. (0.2 g. atom) of magnesium in a total of 150 ml. of ether. Upon decanting through a glass-wool plug into an addition funnel, the material precipitated with the evolution of considerable heat which caused the ether to boil. Upon cooling, the material was dissolved by the addition of 25 ml. of THF. The yield, based on acid titration, was 77%. To 19.0 g. (0.072 mole) of triphenylphosphine in 100 ml. of ether, 0.072 mole of the Grignard reagent was added. The mixture was allowed to stir overnight and was refluxed for 1 hr. Dry oxygen was bubbled through the solution for 3 hr., during which the reaction vessel was cooled by a water bath. A sticky, semi-solid material formed and gathered in one lump. The mixture was poured upon crushed ice containing excess hydrobromic acid. The mixture was filtered to give 1.1 g. of a solid, m.p. 186-190°. The

¹¹²J. Dodanov and H. Medox, Ber., 61, 907 (1928); H. Gilman and G. E. Brown, J. Am. Chem. Soc., 67, 824 (1945); and H. H. Willard, L. R. Perkins, and F. F. Blicke, ibid., 70, 737 (1948).

¹¹³G. Wittig, H. Eggers, and P. Duffner, Ann., 619, 10 (1958).

infrared spectrum indicated that it did not contain the triphenylphosphorus group, so this material was not further investigated. The filtrate was composed of an oil suspended in the aqueous phase. The oil was separated and washed with ether. An attempt to dissolve this material in ca. 2 l. of hot water was unsuccessful. The material dissolved in chloroform. The water used in the attempted crystallization was extracted with chloroform. The extracts were combined with the solution, and the solvent evaporated to give a brown oil. This material, when heated for 15 min. in boiling toluene, solidified to give 5.7 g. (15.2%) of a brown solid, m.p. 190-200°. This material was placed in hot THF and dissolved upon the addition of a few drops of water. The hot solution was treated with decolorizing charcoal, filtered, and cooled to give 3.4 g. (9.1%) of light brown crystals. Recrystallization gave 2.7 g. (7.2%) of solid, m.p. 248-250°. The melting point was unchanged after another recrystallization. The material was thoroughly dried at 100° under 0.5 mm. pressure without loss in weight.

Anal. calcd. for $C_{32}H_{26}BrP$: C, 73.71; H, 5.03; Br, 15.33. Found: C, 73.81, 73.89; H, 4.72, 4.93; Br, 15.76, 16.06.

Preparation of and reaction with benzophenone Two grams (0.04 mole) of (2,2-diphenylvinyl)triphenylphosphonium bromide, suspended in 25 ml. of ether, was treated with 0.004 mole of phenyllithium. The mixture turned a dark red

immediately upon the addition. After 1 hr. of stirring at room temperature, only a small amount of solids remained, which dissolved upon the addition of 75 ml. of THF. To the dark, purplish-brown solution, 0.9 g. (0.005 mole) of benzophenone was added. Subsequent to the removal of the ether by distillation, the mixture was refluxed for 12 hr. and hydrolyzed in dilute acid. The mixture was worked up in the usual fashion and the solvents removed by distillation, yielding a brown, semi-solid material. Treatment with cold ethanol and filtration gave 0.7 g. (53.5%) of impure tetraphenylallene, m.p. 160-165°. Recrystallization from acetone gave 0.6 g. (45.7%) of pure product, m.p. 164-165° (mixed m.p.). The solvent was removed from the mother liquor and the residue crystallized from cyclohexane to give 0.4 g. (40%) of triphenylphosphine oxide, m.p. 154-157° (mixed m.p.).

Attempted Cleavage of

Octaphenylcyclotetrasilane by Diazomethane

Run 1

Diazomethane was prepared from 1.8 g. of Du Pont EXR-101, (70% N,N'-dimethyl-N,N'-dinitrosoterephthalamide) according to directions in the product bulletin. The theoretical yield of diazomethane would be 0.01 mole. The ether-diazomethane distillate was dried for 3 hr. over

potassium hydroxide pellets and redistilled into a mixture of 3.6 g. (0.005 mole) of octaphenylcyclotetrasilane suspended in 50 ml. of THF. The mixture was stirred for 48 hr. and then allowed to stand until the solvents and any unreacted diazomethane had evaporated. The residue was washed with petroleum ether (b.p. 60-70°) and filtered to give 3.3 g. (91.8%) of recovered starting material, m.p. 319-322° (mixed m.p.).

Run 2

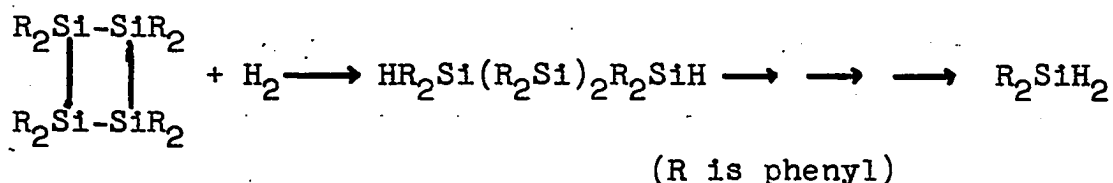
To an undried distillate of ether and diazomethane, prepared as described in Run 1 from 7.1 g. of Du Pont's EXR-101 (theoretical yield of 0.04 mole), there was added 1.0 g. (0.0014 mole) of octaphenylcyclotetrasilane suspended in 50 ml. of benzene. The mixture was stirred for 48 hr. and the volatile material allowed to evaporate. The residue was washed with petroleum ether (b.p. 60-70°) and filtered to give 0.95 g. (95%) of recovered starting material, m.p. 317-320° (mixed m.p.).

DISCUSSION

Hydrogenolysis Reactions

Due to the high reactivity of octaphenylcyclotetrasilane as compared with other compounds containing the disilane linkage, it was considered likely that hydrogenolysis might provide a convenient synthesis of 1,1,2,2,3,3,4,4-octaphenyltetrasilane, resulting from a single cleavage. Although a variety of reaction conditions was used, (see Tables 1 and 2 in the experimental part), none was found which afforded this compound in yields over 12%. Instead, whenever hydrogenolysis was observed, it was accompanied by extensive secondary cleavages leading ultimately to diphenylsilane in yields as high as 50%. There was also obtained material which contained siloxane groups, evidently formed by hydrolysis of silicon-hydrogen bonds by moisture in the system. This is discussed more thoroughly in a subsequent paragraph dealing with reactions of hexaphenyldisilane. However, the direct hydrolysis of the silicon-silicon bonds cannot be completely excluded.

It is probable that 1,1,2,2-tetraphenyldisilane and 1,1,2,2,3,3-hexaphenyltrisilane were also formed, but they could not be isolated. The hydrogenolysis of octaphenylcyclotetrasilane is illustrated in the following equation.



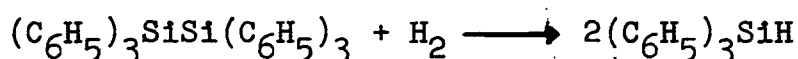
The hydrogenolysis of 1,1,2,2,3,3,4,4-octaphenyltetrasilane itself was not carried out, but there is no reason to suspect that it did not occur as shown in the preceding equation.

The reaction was found to be catalyzed by "copper chromite" or by a mechanical mixture of copper (II) oxide and chromium trioxide (Cr_2O_3). However, palladium on charcoal or Raney nickel were ineffective. No effort was made to exhaust all of the possible types of hydrogenation catalysts.

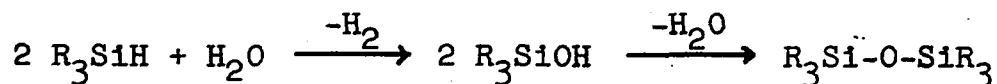
Attempts to effect hydrogenolysis of Compound (B) (dodecaphenylcyclohexane^{87,88} or decaphenylcyclopentasilane^{82,89,90}) were generally without success, although small amounts of diphenylsilane were obtained using "copper chromite" as catalyst. In view of the facts that 1,1,2,2,3,3,4,4-octaphenyltetrasilane, formed initially from the cleavage of octaphenylcyclotetrasilane, undergoes further reaction, and that other organodisilanes, discussed later, also suffer hydrogenolysis, it is not clear why Compound (B) resisted cleavage. It is possible that the conformation of this cyclic compound inhibits the required positioning on the surface of the catalyst. However, the relative unreactivity of this material in other reactions, including

cleavages reported in This Thesis, cannot be omitted as a factor.

The hydrogenolysis reaction was extended to compounds containing only one silicon-silicon bond. Thus, hexaphenyldisilane, when subjected to hydrogen over "copper chromite" catalyst for two hours at 150° and 850 p.s.i.g. pressure, gave a 17% yield of triphenylsilane. In addition to a high



recovery of starting material, there was isolated 10% of hexaphenyldisiloxane (impure). After five hours under similar conditions, no triphenylsilane could be isolated; however, the yield of disiloxane increased. Again, starting material was recovered in high yield. These results are understandable in view of the fact that, in a separate experiment under similar conditions of time, temperature, hydrogen pressure, catalyst, and solvent, triphenylsilane was converted into hexaphenyldisiloxane, with no evidence of recovered starting material being detected. Evidently, silicon-hydrogen bonds were hydrolyzed according to the following, well established reaction.



The amount of water needed for the hydrolysis of the triphenylsilane used was only 0.18 gram (0.01 mole), with

lesser quantities required in the hydrogenolysis reactions. The system used undoubtedly contained sufficient moisture for these reactions to occur. The siloxane formation might also have arisen from oxidation of silicon-hydrogen groups by any oxygen present, or by the direct hydrolysis of silicon-silicon bonds. These possibilities were not explored. The direct oxidation of silicon-hydrogen bonds by the copper oxide present in the catalyst was also considered. However, this reaction is apparently not significant, since triphenylsilane was recovered in good yield after treatment with copper (II) oxide in refluxing xylene for 24 hours, with only a small amount of hexaphenyldisiloxane being formed.

In contrast to the high recovery of hexaphenyldisilane, 1,2-dimethyl-1,1,2,2-tetraphenyldisilane underwent hydrogenolysis to give a 73.4% yield of methyldiphenylsilane after treatment for 2 hr. at 150° and 810 p.s.i.g. pressure in the presence of "copper chromite". This may be due to the higher solubility of starting material in the latter case.

Also, 1,1,2,2-tetramethyl-1,2-diphenyldisilane was cleaved under comparable conditions to give a 21.7% yield of impure dimethylphenylsilane; a mixture of disiloxane and starting material was also obtained. However, hexaethyldisilane, similarly treated, was recovered in high yields, with no evidence of formation of triethylsilane.

Thus, it appears that the disilane bond must be activated

by the presence of phenyl groups for hydrogenolysis to occur. A similar phenomenon has been observed for the cleavage of the aliphatic carbon-carbon bonds in phenyl-substituted ethanes.¹⁹ Thus, pentaphenyl-, 1,1,2,2-, and 1,1,1,2-tetraphenyl-, and even to a small extent 1,1,2-triphenylethane were cleaved by hydrogen over "copper chromite" to give the corresponding phenyl-substituted methanes.¹⁹ Aliphatic compounds were unaffected upon similar treatment. The use of a nickel catalyst afforded the respective cyclohexylethanes, without appreciable cleavage of carbon-carbon bonds except with pentaphenylethane,¹⁹ which may be due to dissociation into free radicals.

As mentioned previously, Raney nickel was ineffective in bringing about the cleavage of octaphenylcyclotetrasilane. Furthermore, 1,1,2,2-tetraphenyldisilane and 1,2-dimethyl-1,1,2,2-tetraphenyldisilane were recovered in high yields when treated with hydrogen under 800 p.s.i.g. pressure for 3 hr. at 150° over Raney nickel. Even under the more forcing conditions, 220° and 1630 p.s.i.g. of hydrogen pressure for 11 hr. in the presence of a more active form of Raney nickel, (W-5), 1,2-dimethyl-1,1,2,2-tetraphenyldisilane was recovered in a yield of 69.4%. A small amount of product was obtained which contained silicon-hydrogen bonds, while the remainder of the material showed a strong absorption band characteristic of the siloxane grouping in its infrared spectrum. Both of these fractions also contained

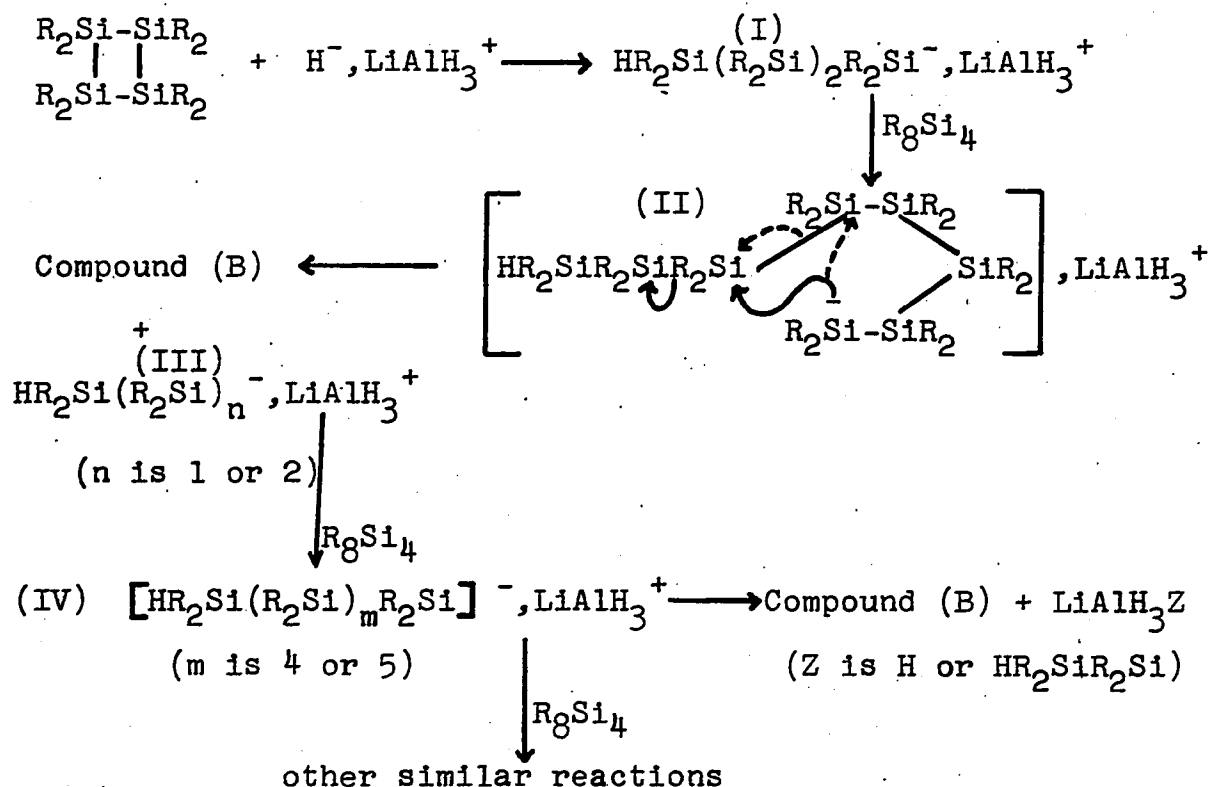
phenyl and cyclohexyl and/or cyclohexenyl groups. To make sure that the catalyst was active and that the solvent did not contain a catalyst poison, the same reagents were used to successfully hydrogenate tetraphenylsilane to give the corresponding tetracyclohexyl derivative.⁸ A small amount of cleavage of silicon-carbon bonds was observed, as indicated by the presence of infrared absorption bands characteristic of silicon-hydrogen groups in the spectrum of the material obtained from the mother liquor.

Since the series of methylphenyl-substituted monosilanes has been hydrogenated over a Raney nickel catalyst to give the corresponding cyclohexyl derivatives,⁸ it does not seem likely that the presence of methyl groups in 1,2-dimethyl-1,1,2,2-tetraphenyldisilane should cause the apparent inability of this compound to undergo hydrogenation. Therefore, it seems that one of the methyldiphenylsilyl groups prevents the aromatic nuclei on the other from undergoing hydrogenation. The exact mode of this inhibition is not clear. Perhaps steric factors prevent the proper adsorption on the catalytic surface.

Apparently, the disiloxane group is quite stable towards hydrogenolysis, as hexaphenyldisiloxane was recovered nearly quantitatively after treatment at 150° for two hours under 800 p.s.i.g. of hydrogen pressure in cyclohexane with "copper chromite" as catalyst. There was no evidence of the formation of triphenylsilanol or triphenylsilane.

Cleavages by Lithium Aluminum Hydride and Related Reactions

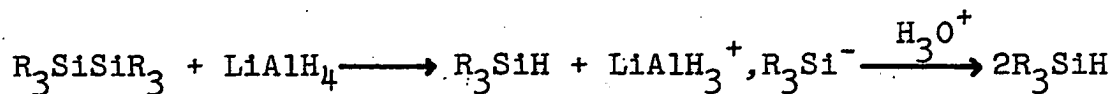
Octaphenylcyclotetrasilane was found to be converted into Compound (B) (dodecaphenylcyclohexasilane^{87,88} or deca-phenylcyclopentasilane^{82,89,90}) in a 64% yield upon treatment with lithium aluminum hydride in tetrahydrofuran after twenty hours at room temperature. It seems likely that the mechanism involved in this reaction is analogous to that proposed for this same transformation by organometallic compounds,^{89,90,93} including silylmetallic reagents.^{93,94} The proposed mechanism is shown in the following reaction scheme. The fact that -



(R is phenyl; Compound (B) is a five- or six-membered ring)

Compound (B) was recovered in a 74% yield after similar treatment with lithium aluminum hydride is consistent with the accumulation of this compound in the preceding reaction. Further support for this mechanistic pathway was obtained by the isolation of products containing one, two, three, four, and five (or six) diphenylsilylene units, corresponding to hydrolysis of intermediate complexes such as (I), (III), and (IV), from these and subsequent reactions of octaphenylcyclotetrasilane and Compound (B) with lithium aluminum hydride, (see Table 6 in the experimental part). Other evidence related to this reaction was obtained during an investigation on the nature and scope of the cleavage of silicon-silicon bonds by lithium aluminum hydride in tetrahydrofuran.

The series of compounds, hexaphenyldisilane, 1,2-dimethyl-1,1,2,2-tetraphenyldisilane, 1,1,2,2-tetramethyl-1,2-dipenyldisilane, and hexaethyldisilane was treated with lithium aluminum hydride in refluxing tetrahydrofuran for comparable lengths of time, (see Table 5 in the experimental section). The general reaction is illustrated in the following equation. The yields of the corresponding products

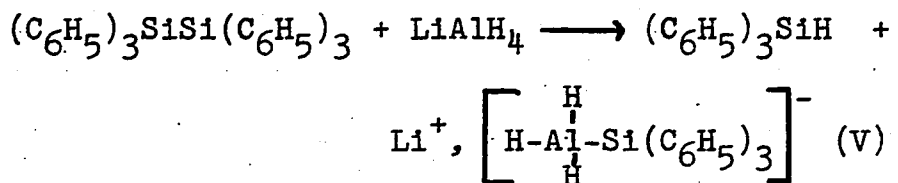


decreased, respectively, as the number of phenyl substituents decreased, with no triethylsilane being detected from hexa-

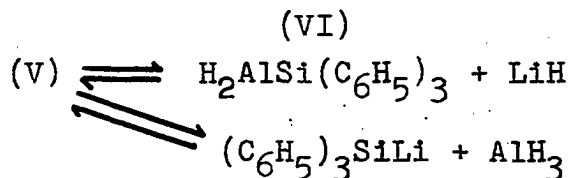
ethyldisilane. 1,1,1-Trimethyl-2,2,2-triphenyldisilane also reacted with lithium aluminum hydride in tetrahydrofuran, with trimethylsilane being obtained by distillation from the reaction mixture prior to hydrolysis, and triphenylsilane being isolated after hydrolysis. These reactions closely parallel the cleavage of organodisilanes by lithium metal in tetrahydrofuran.^{41,50} Both reactions occur only with phenyl-substituted disilanes, evidently due to stabilization of the resulting anions by aromatic nuclei. The one exception to this is the formation of silylpotassium, H_3SiK , from the reaction of silane with potassium or from the cleavage of disilane by potassium hydride in ethylene glycol dimethyl ether.²⁷ The latter reaction is closely related to the cleavages by lithium aluminum hydride.



The nature of the intermediate complexes, represented previously by the formula, $\text{LiAlH}_3^+, \text{R}_3\text{Si}^-$, was investigated thoroughly in the reactions involving hexaphenyldisilane, as shown in the following equation. Evidence which strongly



supports the structure (V) was obtained from the following experiments. The possible equilibrium product (VI) was not eliminated, nor could the presence of a small amount of triphenylsilyllithium be excluded by the means employed.



The initial formation of triphenylsilane by attack of hexaphenyldisilane by hydride was established by use of lithium aluminum deuteride, followed by hydrolysis in hydrochloric acid. The ratio of triphenylsilane-d to triphenylsilane was not the theoretical 1:1, but the formation of deuterated product is significant. The variation from the theoretical ratio will be discussed later. The total yield of triphenylsilanes was 75.3%.

The formation of triphenylsilane by the hydrolysis of any triphenylsilyllithium present in the reaction mixture was precluded by carbonation of the reaction mixture and also by treatment with chlorotrimethylsilane. Both of these reagents are known to react readily with triphenylsilyllithium under the conditions employed.^{41,43} Yet, subsequent to acid hydrolysis in these reactions, greater than 50% yields of triphenylsilane were obtained, based on hexaphenyldisilane.

Apparently, a silylaluminum compound does not react appreciably with carbon dioxide at the temperature of Dry Ice, an unreactivity also observed with other organoaluminum compounds.¹¹⁴ The yield of triphenylsilane subsequent to carbonation and acid hydrolysis was 60%. There was also obtained some products containing silanol and siloxane groups. The formation of these materials can arise primarily from two sources. Under the conditions of carbonation, atmospheric moisture condensed on the reaction mixture and could have caused hydrolysis of silicon-hydrogen bonds. This would account for the lower yield of triphenylsilane isolated from this reaction as compared to other reactions. However, these results can be equally well accounted for if there was some triphenylsilyllithium present in the mixture prior to carbonation. Although no triphenylsilylcarboxylic acid was isolated, this compound is known to undergo decarbonylation to yield triphenylsilanol¹¹⁵ which can condense to the disiloxane. Since a greater than 50% yield

¹¹⁴The chemistry of organoaluminum compounds has recently been reviewed: K. Ziegler, "Organo-aluminum Compounds", in H. Zeiss, ed., "Organometallic Chemistry", pp. 194-269, Reinhold Publishing Corporation, New York, N.Y., 1960; G. E. Coates, "Organo-metallic Compounds", 2nd ed., John Wiley and Sons, Inc., New York, N.Y., 1960, pp. 126-144.

¹¹⁵A. G. Brook and H. Gilman, J. Am. Chem. Soc., 77, 2322 (1955).

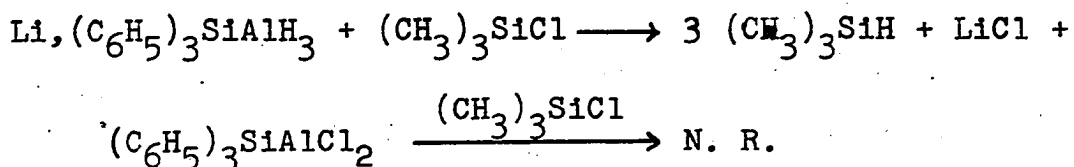
of triphenylsilane was isolated, this sequence of reactions establishes the formation of a silylaluminum compound, but cannot completely rule out the presence of some triphenylsilyllithium.

Triphenylsilane was isolated in yields of 60% and 78% after treatment of reaction mixtures with chlorotrimethylsilane, followed by hydrolysis. Although no 1,1,1-trimethyl-2,2,2-triphenyldisilane could be found, the presence of some triphenylsilyllithium cannot be completely excluded since triphenylsilane was not obtained quantitatively. However, the yields obtained in this case are of the same order isolated upon acid hydrolysis alone. Therefore, these results indicate that if an equilibrium between (V) and triphenylsilyllithium exists, only small amounts of silyllithium are present.

There was some concern as to whether or not all of the triphenylsilane was formed in the reaction mixture prior to hydrolysis. For example, the reaction mixture obtained from triphenylsilyllithium and aluminum chloride, a method used for the preparation of other organoaluminum compounds, was hydrolyzed in deuteriochloric acid. The infrared spectrum of the triphenylsilane obtained showed only a very weak absorption band characteristic of silicon-deuterium bonds. Also, triphenylsilane has been isolated in yields of up to 30% upon anhydrous work-up of the reaction mixtures resulting from the treatment of various metal halides with

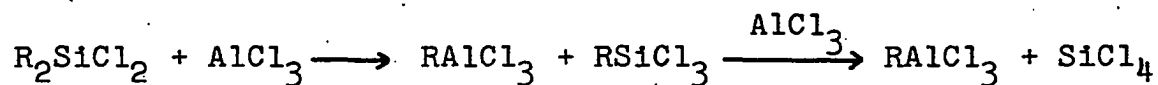
triphenylsilyllithium in tetrahydrofuran.⁷¹ However, the presence of a triphenylsilyl anion in the cleavage by lithium aluminum hydride was confirmed by hydrolysis in deuteriochloric acid, subsequent to treatment with chlorotrimethylsilane, and the identification of substantial amounts of triphenylsilane-d.

The fact that a lithium organosilylaluminum hydride complex is capable of reacting with silicon-silicon bonds in the reaction involving octaphenylcyclotetrasilane and yet not react with chlorotrimethylsilane requires some explanation. It appears likely that the latter reaction takes the course illustrated in the following equation. By



analogy, a compound of the type $\text{R}_3\text{SiAlCl}_2$ would not be expected to react readily with chlorotrimethylsilane under the mild conditions of refluxing in tetrahydrofuran (b.p. 65°), since trimethylaluminum has been shown not to react with silicon tetrachloride or with dichlorodimethylsilane at 130°, ¹¹ and temperatures between 140-250° were used to alkylate silicon halides with trialkylaluminum compounds

and with the less reactive mono- and dialkylaluminum chlorides.¹¹⁶⁻¹¹⁸ Furthermore, the reaction of aluminum chloride with organosilicon halides in the absence of solvents has been shown to occur with the formation of organoaluminum compounds and higher halides of silicon, as illustrated in the following equation.¹¹⁹



The reactivity of the silylaluminum complex in the cleavage of silicon-silicon bonds may be indicative of the nature of the complex. Compounds of the type LiAlR_4 have been observed to have an initial reactivity comparable to that of organolithium compounds.¹¹⁴ Thus, an intermediate of the type $\text{LiAlH}_3(\text{SiR}_3)$ would explain the observed results.

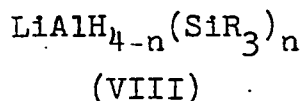
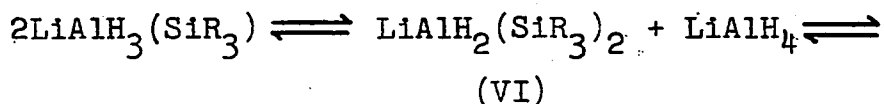
The following equation illustrates a possible equilibrium hitherto not mentioned. Evidence suggesting that

¹¹⁶B. Lengyel and T. Székely, Z. anorg. u. allgem. Chem., 287, 273 (1956).

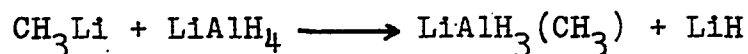
¹¹⁷H. C. Brown, U. S. Patent 2,762,824, Sept. 11, 1956; [C. A., 51, 7412 (1957)].

¹¹⁸Kali-Chemie A.-G., British Patent 756,612, Sept. 5, 1956; [C. A., 51, 8776 (1957)].

¹¹⁹A. Y. Yakubovich and G. V. Motsarev, Zhur. Obshchei Khim., 23, 771 (1953); [Original available but not translated; translated in J. Gen. Chem. U.S.S.R., 23, 805 (1953)].



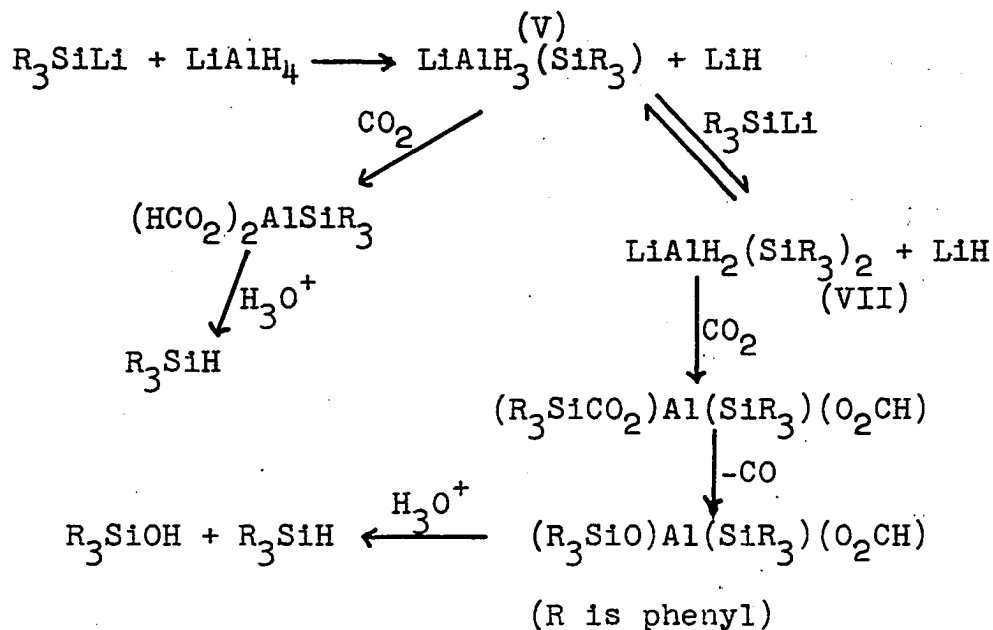
this type of reaction is not significant was obtained from reactions of triphenylsilyllithium with lithium aluminum hydride. The reaction of metal alkyls with lithium aluminum hydride has been shown to yield alkylaluminum compounds and metallic hydrides.¹²⁰ Methyllithium apparently reacts according to the following equation. The analogous reaction between triphenylsilyllithium and lithium aluminum hydride,



in a 1:1 mole ratio, followed by carbonation and acid hydrolysis, yielded 73.1% of triphenylsilane. Similar treatment of the mixture obtained from adding triphenylsilyllithium to lithium aluminum hydride in a 2:1 mole ratio, respectively, resulted in only a 43% yield of triphenylsilane. A reasonable explanation of these results is shown

¹²⁰G. D. Barbaras, C. Dillard, A. E. Finholt, T. Wartik, K. E. Wilzbach, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **73**, 4585 (1951); T. Wartik and H. I. Schlesinger, *ibid.*, **75**, 835 (1953).

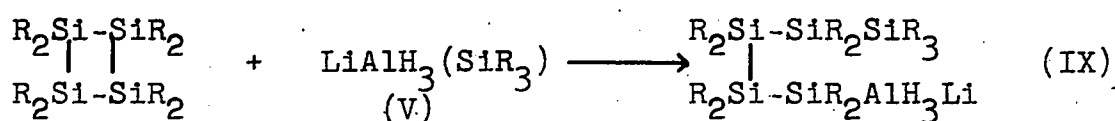
in the following sequence of equations. If the intermediate



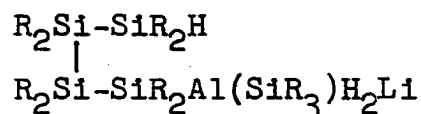
silylaluminum complex in the cleavage of silicon-silicon bonds by lithium aluminum hydride was of the type (VII), the yield of triphenylsilane would not have exceeded 50%. Since higher yields were obtained, it is reasonable to conclude that the intermediates have the formula $\text{LiAlH}_3(\text{SiR}_3)$. In fact, there is reason to suspect that a compound of the type (VII) is unstable or is not even formed by the reaction shown in the preceding equation, since acid hydrolysis alone of the mixture obtained from adding triphenylsilyllithium to lithium aluminum deuteride in a 2:1 mole ratio, respectively, gave only a 34.6% yield of triphenylsilane, some of which was deuterated. The mode of formation of silicon-deuterium bonds in this reaction is not clear. However,

related reactions are discussed later. The fate of the second equivalent of triphenylsilyllithium is not known, but may involve reaction with solvent.

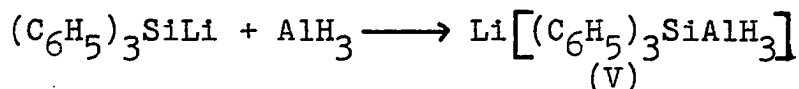
The reaction of octaphenylcyclotetrasilane with lithium aluminum hydride requires that the proposed silylaluminum complex be capable of cleaving silicon-silicon bonds. To establish that such a complex would react with octaphenylcyclotetrasilane, the mixture obtained from the complete cleavage of hexaphenyldisilane by a one molar equivalent of lithium aluminum hydride was allowed to react with the cyclic tetrasilane. In addition to a 45% recovery of octaphenylcyclotetrasilane, Compound (B) was obtained in a 55% yield (based on unrecovered starting material). No products containing the triphenylsilyl group bound to silicon could be isolated from the resulting complex mixture of products. This would have established the proposed first step in this reaction, as illustrated below. Since



indications are that compounds of the type $\text{LiAlH}_2(\text{SiR}_3)_2$ are not formed or are not stable suggests that the initial cleavage forms a silicon-silicon bond and not a silicon-hydrogen bond, which would lead to the intermediate shown in the following diagram. Negative evidence supporting this



hypothesis is the fact that triphenylsilane was obtained in only a 50% yield, based on the hexaphenyldisilane used. A possible alternate synthesis of the above complex, (V), by the reaction of triphenylsilyllithium and aluminum hydride, also gave similar results with octaphenylcyclotetrasilane. This synthetic approach to (V) was not investigated completely and is therefore only indicative.



In an attempted preparation of tris(triphenylsilyl)-aluminum from the reaction of triphenylsilyllithium and freshly sublimed aluminum chloride, there was obtained a nearly colorless solution. A portion of this solution was withdrawn and hydrolyzed in deuteriochloric acid. Work-up yielded triphenylsilane which contained only a small amount of deuterated product, as indicated by its infrared spectrum. The remainder of the solution had been refluxed with octaphenylcyclotetrasilane. Since the hydrolysis reaction had indicated that little silylaluminum compound remained, it was not surprising that the cyclic tetrasilane was recovered in almost quantitative amounts. Work-up of the main body of the reaction mixture gave only 20% of triphenylsilane.

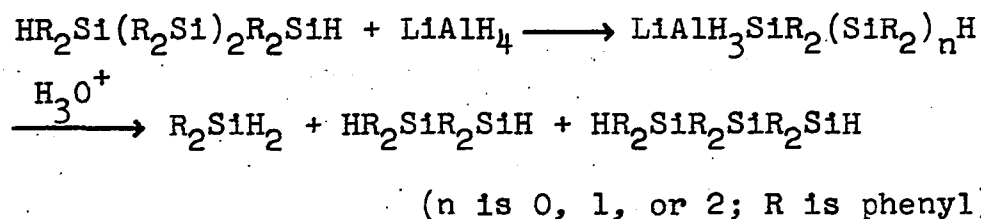
The exact nature of the formation of silicon-hydrogen groups prior to hydrolysis was not investigated. Some intractable oils were also obtained from this reaction mixture, the infrared spectra of which contained absorption bands characteristic of aliphatic carbon-hydrogen bonds, indicative of reaction with the solvent.

The formation of some triphenylsilane, from sources other than hydride and hydrolysis of silylaluminum compounds, was also indicated in the cleavage of hexaphenyldisilane by lithium aluminum hydride. For example, the ratio of triphenylsilane to deuterated product, upon hydrolysis in deuteriochloric acid, was not the theoretical 1:1. The ratio of SiH to SiD in this case was of the order 3:2, while that obtained from the cleavage by lithium aluminum deuteride followed by hydrolysis in hydrochloric acid was nearly the reverse. Any significant exchange of hydrogen between triphenylsilane and the aqueous media is precluded by a previous observation¹²¹ in which no silicon-hydrogen absorption bands were present in the infrared spectrum of triphenylsilane-d prepared by the reduction of the chloride with lithium aluminum deuteride, followed by hydrolysis in hydrochloric acid. However, it was established that hy-

¹²¹H. Gilman and E. A. Zuech, Chemistry Department, Iowa State University of Science and Technology, Ames, Iowa. Observation from a study on organosilicon hydrides, private communication, 1959.

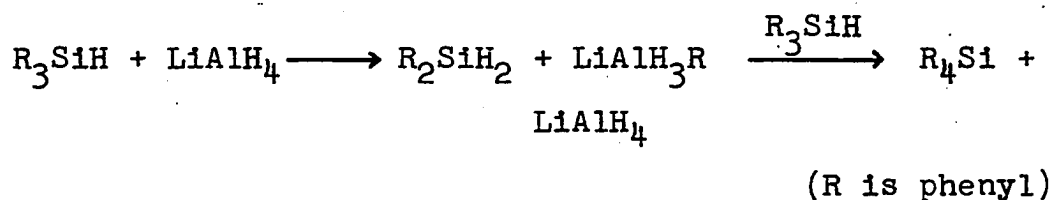
dride-deuteride exchange does occur between triphenylsilane and lithium aluminum deuteride in refluxing tetrahydrofuran. Thus, a larger than the theoretical amount of deuterated product would result if a portion of silylmetallic complex were to react (with solvent) to give triphenylsilane, which could subsequently exchange with deuteride ion. In the cleavage by lithium aluminum hydride, the triphenylsilane obtained from both sources would be constant upon hydrolysis in deuteriochloric acid, with only the remaining silyl-aluminum complex being deuterated. This type of reaction would also account for the formation of some triphenylsilane-d from the reaction between triphenylsilyllithium and lithium aluminum deuteride, followed by acid hydrolysis.

In addition to the compounds already mentioned, 1,1,-2,2,3,3,4,4-octaphenyltetrasilane and the corresponding 1,4-dichloride were cleaved by lithium aluminum hydride in tetrahydrofuran. From these reactions, there was isolated compounds containing one, two, three, and four diphenylsilylene units, as is illustrated in the following equation.



From the lithium aluminum hydride cleavages of hexaphenyldisilane, there was always formed a small amount of

diphenylsilane, showing that under the conditions of refluxing in tetrahydrofuran, some cleavage of silicon-phenyl groups had occurred. This was also observed in the reaction of triphenylsilane with lithium aluminum hydride under similar conditions. In addition to recovered triphenylsilane, there was obtained about 3% of diphenylsilane and a lesser amount of tetraphenylsilane. A mechanism for this reaction is illustrated in the following equation.



A redistribution reaction catalyzed by possible traces of aluminum chloride in the lithium aluminum hydride was considered unlikely since these react to give aluminum hydride and lithium chloride.¹⁰⁴ In addition, evidence presented later shows that aluminum chloride catalyzed reactions do not occur readily in tetrahydrofuran. An attempted cleavage of tetraphenylsilane by lithium aluminum hydride did not afford triphenylsilane in a detectable quantity and starting material was recovered in a 96% yield.

The attempted reaction of octaphenylcyclotetrasilane and other compounds with lithium aluminum hydride in diethyl ether was unsuccessful. Thus, this solvent may be used in the reduction of polysilane halides without effecting silicon-silicon bond fission. For example, the reduction of chloro-

pentaphenyldisilane has been shown to proceed normally.¹²²

In addition, hexaphenyldisilane was unaffected when treated with lithium aluminum hydride in pyridine.

Sodium hydride in refluxing tetrahydrofuran also converted octaphenylcyclotetrasilane into Compound (B) in a 77% yield. Lithium hydride was much less effective, yielding only a small amount of Compound (B). From this reaction, starting material was recovered in good yield. Compound (B) was unaffected by these two metallic hydrides. Neither of the cyclic-perphenylated polysilanes was reduced by sodium borohydride in boiling dioxane. Similar results were obtained using mixed aluminum chlorohydrides, prepared in tetrahydrofuran from the reaction of aluminum chloride with sodium hydride or with lithium aluminum hydride. However, the apparent unreactivity of the metal hydride-aluminum chloride systems may well be due to cleavage of the tetrahydrofuran, a reaction which has recently been observed to give n-butanol, subsequent to hydrolysis.¹²³ Tetrahydrofuran did not react with lithium aluminum hydride in the absence of aluminum chloride.

¹²²H. Gilman and J. J. Goodman, J. Am. Chem. Soc., **75**, 1250 (1953).

¹²³W. J. Bailey and F. Marktscheffel, J. Org. Chem., **25**, 1797 (1960).

Attempted Cleavages by Other Reducing Agents

Octaphenylcyclotetrasilane and Compound (B) were treated with: zinc amalgam and hydrochloric acid; sodium amalgam in acetic acid; hydriodic acid and red phosphorus; and aluminum isopropoxide. These attempted reductions were not successful. The cyclic organosilicon compounds were usually recovered in high yields and there was no evidence of products containing silicon-hydrogen bonds. The reaction conditions are given in Table 8 in the experimental part.

It is interesting to note that in the reactions involving hydriodic acid and red phosphorus, silica containing some silicic acid was apparently formed. It is possible that reduction of the silicon-silicon bonds occurred, followed by hydrolysis of the silicon-hydrogen groups and cleavage of the phenyl substituents. However, this need not be the case, since hydriodic acid alone converted octaphenylcyclotetrasilane into silica under similar conditions.

Reactions with Metals

Hexaphenyldisilane by lithium in the presence of methyl phosphate

The cleavage of octaphenylcyclotetrasilane and other polysilanes by lithium in tetrahydrofuran frequently leads to complex mixtures of products due to reactions of the

silyllithium compounds with silicon-silicon bonds.^{89,90,93} Since it has been established that silyllithium compounds can be alkylated with trialkyl phosphates,¹²⁴ the possibility of running the cleavages in the presence of methyl phosphate was investigated as a means of derivatizing the silyllithium compounds in situ, and thereby deterring side reactions.

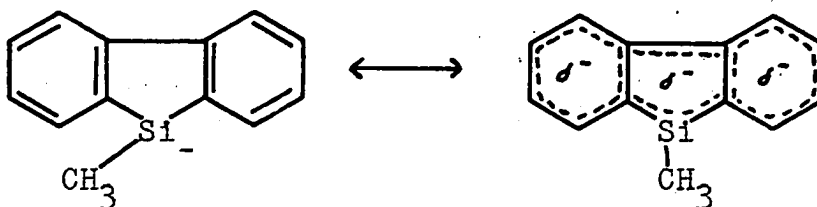
Preliminary reactions with hexaphenyldisilane were not promising. Although the expected methyltriphenylsilane was obtained in low yields, the reactions did not follow a smooth course. After initiation of the cleavage, the reaction seemed to stop. Reinitiation occurred only after prolonged stirring, and was unpredictable. A rather complex mixture resulted, evidently due to secondary cleavages of silicon-carbon groups, as indicated by low-boiling products containing silicon-hydrogen groups being obtained after acid hydrolysis.

Attempted cleavages of silicon-silicon bonds

The standard method of preparing organosilylmetallic compounds is by cleavage of silicon-silicon bonds by alkali metals.² Although fission by other metals has not been reported, the reactivity of octaphenylcyclotetrasilane presented the possibility of cleavage by magnesium, leading

¹²⁴H. Gilman and B. J. Gaj, ibid., 26, 2471 (1961).

to the first established preparation of a solution containing a silyl-Grignard reagent. However, no reaction could be effected with magnesium or with a mixture of magnesium and magnesium iodide in ether or in tetrahydrofuran. An unsuccessful attempt to prepare bis(triphenylsilyl)magnesium by the cleavage of hexaphenyldisilane by magnesium in tetrahydrofuran has been previously reported.⁵⁰ It was hoped that the use of a mixture of magnesium and magnesium iodide would result in the formation of triphenylsilylmagnesium iodide, but no reaction was observed. Similar results were obtained with 5,5'-dimethyl-5,5'-bi-(dibenzosilole), although the resulting anion might have had resonance stabilization, as illustrated in the following diagram.



In addition, no reaction was observed between aluminum metal and hexaphenyldisilane in refluxing tetrahydrofuran.

Reactions of organosilicon halides

Lithium

Dichloromethylphenylsilane

A number of reactions between dichloromethylphenylsilane and lithium in tetrahydro-

furan was carried out in attempts to synthesize cyclic compounds analogous to those obtained from dichlorodiphenylsilane. However, no well defined crystalline products were isolated. Only small amounts of solids with wide melting point ranges were obtained, in addition to large quantities of viscous, intractable oils. Some of these oils partially solidified into resinous semi-solids. Either the reaction led primarily to polymer formation or the cyclic methylphenyl-substituted compounds were liquids or low melting solids which could not be caused to crystallize.

Chlorotriphenylsilane in the presence of methyl phosphate An attempt to capture triphenylsilyllithium in the "direct" synthesis, without the coupling to and cleavage of hexaphenyldisilane, was carried out by running the reaction in the presence of methyl phosphate. Although the reaction mixture became quite warm in the initial stage, the reaction appeared to stop with the addition of more chlorotriphenylsilane. Upon work-up, products primarily from the hydrolysis of the chloride were obtained. Only traces of methyltriphenylsilane were isolated and none of the coupling product was found. The low yield of methyltriphenylsilane does not allow any conclusion as to the method of its formation. It most likely came from triphenylsilyllithium reacting with methyl phosphate. Whether the triphenylsilyllithium arose from the "direct" reaction with the chloride or from cleavage of hexaphenyldisilane

cannot be ascertained. Although methyl phosphate was found not to react appreciably with lithium in tetrahydrofuran at room temperature, it is possible that some methyl-lithium could arise in this fashion and react with chlorotriphenylsilane to give the same product. A reaction between magnesium and methyl phosphate in tetrahydrofuran to give a methylmagnesium phosphate which reacted with chlorotriphenylsilane has recently been observed.¹²⁵

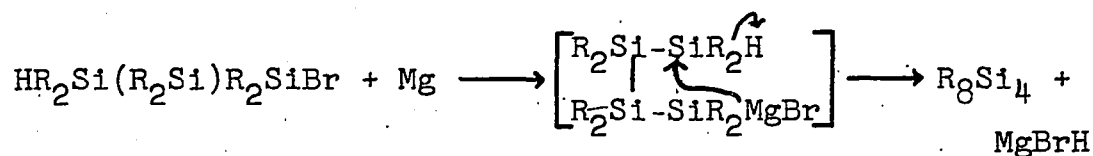
Aluminum (attempted) The attempted reaction between metallic aluminum and chlorotriphenylsilane in refluxing tetrahydrofuran did not afford the easily isolable coupling product, hexaphenyldisilane, nor was triphenylsilane obtained upon acid hydrolysis. Identical results were obtained after treatment in the same solvent at high temperatures in a pressure vessel. Thus, the direct synthesis of a silyl-aluminum compound does not appear to be feasible.

Magnesium The reaction between 5-chloro-5-methyldibenzosilole and excess magnesium was considered as a possible synthesis of a silyl-Grignard reagent, due to potential stabilization of the resulting anion, as illustrated in the diagram on page 133. However, only the coupling product was obtained. Throughout the course of

¹²⁵H. Gilman and W. H. Atwell, Chemistry Department, Iowa State University of Science and Technology, Ames, Iowa. Results from studies on organometallic compounds, private communication, 1961.

the reaction, the possible presence of detectable organo-metallic compounds was monitored by intermittent color tests, which were all negative.

In attempted syntheses of hexadecaphenyloctasilane by coupling 1-bromo-1,1,2,2,3,3,4,4-octaphenyloctasilane with magnesium, positive Color Tests I were obtained, which is usually indicative of the presence of organometallic reagents. Attempts to derivatize any such compounds were unsuccessful. Also, no octasilane could be isolated from the resulting complex mixture of products. However, octaphenylcyclotetrasilane and Compound (B) were obtained, in addition to small amounts of 1,1,2,2,3,3,4,4-octaphenyloctasilane and the homologous decaphenylpentasilane. The formation of octaphenylcyclotetrasilane suggests that the following reaction has taken place, at least in part. The positive



(R is phenyl)

Color Tests I⁷⁵ obtained in this reaction were blue instead of the usual green. Since metallic hydrides give positive color tests which are blue, it is likely that the magnesium bromohydride formed in this reaction was responsible for the tests obtained. Magnesium bromohydride could also be

formed in reactions of the proposed intermediate silyl-Grignard reagents with other silicon-hydrogen groups. Compound (B) could arise by reactions similar to those involving other organometallic reagents previously described, while the formation of the other products could result from coupling reactions with intermediate bromides or from the reduction of silicon-silicon or silicon-bromine groups by magnesium bromohydride. In view of the fact that 1,1,2,2,3,3,4,4-octaphenyltetrasilane was obtained subsequent to the addition of methyl phosphane, it is unlikely that silicon-hydrogen bonds were formed by hydrolysis of intermediate silylmagnesium halides.

The attempted coupling of 1-bromo-1,1,2,2,3,3,4,4-octaphenyltetrasilane by sodium in xylene did not afford any of the octasilane either. A small amount of octaphenylcyclotetrasilane was obtained, in addition to a complex mixture of products containing siloxane and/or silanol groups, as indicated by infrared analyses.

The reaction of 1-chloro-1,1,2,2-tetraphenyldisilane with magnesium in tetrahydrofuran proceeded normally to give the corresponding tetrasilane in a 51% crude yield.

Pyrolysis Reactions of Cyclic Polysilanes

The reaction of dichlorodiphenylsilane with alkali metals leads to a third compound, in addition to octaphenylcyclotetrasilane and Compound (B). This material, formed

in low yields, was labeled Compound (C) by Kipping and is presumably a higher cyclic homolog. As was mentioned previously, the structure of Compound (B) is being re-investigated as to the possibility of it being a five-membered ring. If this should prove to be the case, it is reasonable to suspect that Compound (C) may be the six-membered ring compound.

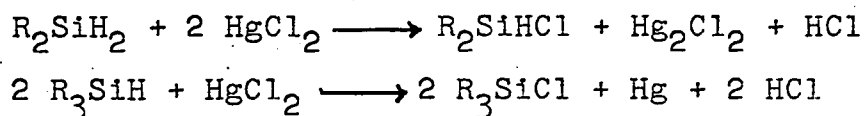
Kipping had reported⁸⁴ that heating of Compound (B) resulted in the formation of glue-like materials, but did not specify the exact reaction conditions. It was considered that pyrolysis of octaphenylcyclotetrasilane and Compound (B) under an inert atmosphere might lead to the formation of Compound (C) in appreciable quantities. However, this was not realized, with primarily polymeric-like substances being formed in addition to small amounts of materials containing silicon-hydrogen groups, evidently formed by free radical reactions.

Preparation of Organosilicon Chlorides from the Corresponding Hydrides

The conversion of silicon-hydrogen bonds into the corresponding halides in organopolysilanes by reaction with halogens has the disadvantage that silicon-silicon bond fission may also occur. Although 1,2-dichloro-1,1,2,2-tetraphenyldisilane has been prepared in good yield from the dihydride by reaction with chlorine,^{36b} an attempt to effect

a similar halogenation of 1,2-dimethyl-1,2-diphenyldisilane resulted in silicon-silicon bond cleavage. These reactions are in accord with the previous observations that hexaaryl-disilanes react only slowly with halogens,^{45,47,126} but hexaalkyldisilanes are cleaved quite readily.^{51,127}

It has been demonstrated that mercuric chloride efficiently converts low-boiling, liquid organosilicon hydrides into the chlorides,¹²⁸ as illustrated in the following equations. The use of mercuric chloride in the halogenation



of organopolysilanes would have the advantages of a controlled halogen source and a mild reagent which might not cleave disilane bond. These advantages were demonstrated in the monochlorination of 1,1,2,2-tetraphenyldisilane which afforded around 50% of 1-chloro-1,1,2,2-tetraphenyldisilane. However, the attempted monochlorination of 1,2-dimethyl-1,2-diphenyldisilane and dichlorination of 1,1,2,2,3,3,4,4-

¹²⁶F. S. Kipping, *J. Chem. Soc.*, 119, 647 (1921); H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, 75, 3762 (1953); H. Gilman and G. E. Dunn, *ibid.*, 73, 5077 (1951).

¹²⁷M. Kumada, J. Nakajima, M. Ishikawa, and Y. Yamamoto, *J. Org. Chem.*, 23, 292 (1958); M. Kumada and M. Yamaguchi, *J. Chem. Soc., Japan*, 57, 175 (1954).

¹²⁸H. H. Anderson, *J. Am. Chem. Soc.*, 80, 5083 (1958); *ibid.*, 81, 1027, 4785 (1959); *ibid.*, 82, 1323 (1960).

octaphenyltetrasilane did not proceed satisfactorily. All of these reactions were carried out in solvents such as ether, benzene, and tetrahydrofuran. Triphenylsilane had previously been converted into the chloride in a 66% yield upon reaction with mercuric chloride in tetrahydrofuran.⁷¹ This reaction was repeated using different solvents in an effort to establish the best reaction conditions. Chlorotriphenylsilane was obtained in yields of 30%, 40%, and 72% upon reaction in benzene, ether, and tetrahydrofuran, respectively, indicating that tetrahydrofuran is the preferred solvent under mild conditions. This is perhaps due to the high solubility of mercuric chloride in this solvent. However, the use of tetrahydrofuran may be limited to mild conditions, since the hydrogen chloride formed in the reaction may cleave the solvent upon heating to yield 4-chloro-1-butanol¹²⁹ which could react with the organosilicon halide.

Recently, the use of phosphorus pentachloride as a source of chloride in this type of reaction has shown considerable promise, and was found to be effective with 1,2-dimethyl-1,2-diphenyldisilane and perphenylated polysilanes.¹³⁰

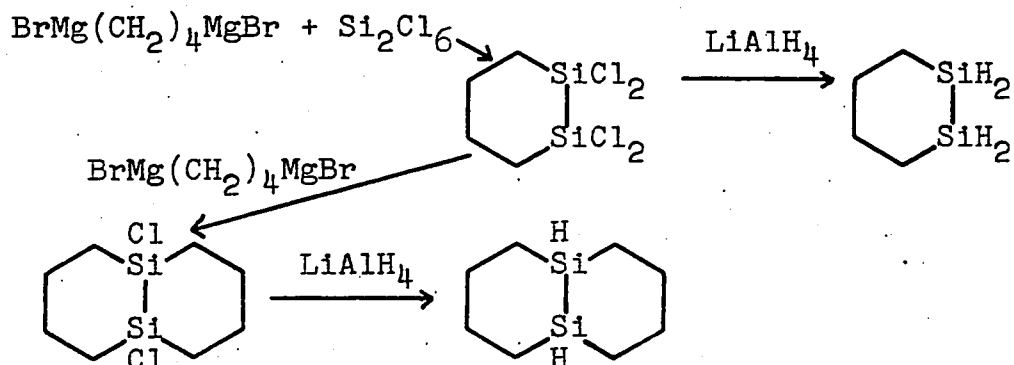
¹²⁹D. Starr and R. M. Hixon, J. Am. Chem. Soc., 56, 1595 (1934).

¹³⁰H. Gilman, S. Cooper, and G. Chainani, Chemistry Department, Iowa State University of Science and Technology, Ames, Iowa. Results from halogenation studies, private communication, 1961.

Reaction of Tetramethylenedimagnesium

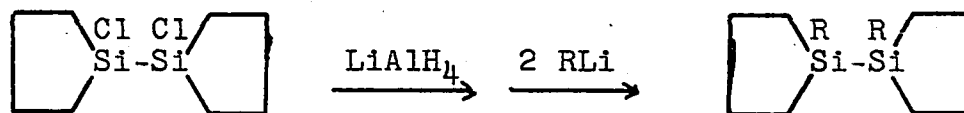
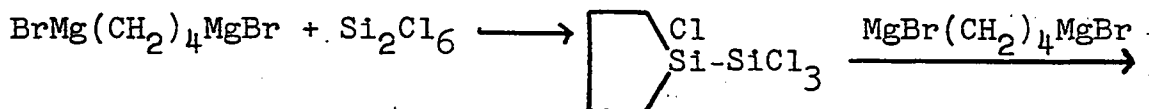
Bromide with Hexachlorodisilane

The reaction between hexachlorodisilane and tetramethylenedimagnesium bromide was briefly investigated as a possible synthetic approach to silicon analogs of cyclohexane and decahydronaphthalene containing the disilane linkage, as illustrated in the following reactions.



Compounds containing the disilacyclohexane ring have been prepared by analogous reactions involving symmetrically-substituted dihalodisilanes.^{76,109} The crude reaction mixtures were reduced with lithium aluminum hydride to obviate the necessity of handling the easily hydrolyzable chlorides. It was realized that a mixture of products could arise, but it was hoped that the formation of six-membered rings might be favored and result in a high proportion of the desired compounds. However, the only product isolated in appreciable amounts contained five-membered rings, as established by derivatization with phenyllithium to give a

known compound. These reactions are illustrated in the following equations. It is evident that the formation of



(R is phenyl)

five-membered rings occurs readily and is more favored than the cyclization to six-membered rings in this reaction. In a previous attempt to prepare an analogous six-membered ring compound by the reaction of 2,2'-dilithiobiphenyl with 1,2-dibromo-1,1,2,2-tetraphenyldisilane, cleavage of the silicon-silicon bond occurred with the formation of a five-membered ring including only one silicon atom.^{131,132} A similar cleavage-cyclization reaction has also been observed in an attempt to synthesize a seven-membered ring containing

¹³¹H. Gilman and E. A. Zuech, Chemistry Department, Iowa State University of Science and Technology, Ames, Iowa. Results from a study on cyclic organosilicon compounds, private communication, 1960.

¹³²For a discussion of the cleavage of silicon-silicon bonds by organometallic compounds, see H. Gilman and G. D. Lichtenwalter, J. Org. Chem., 24, 1588 (1959).

the tetraphenyldisilane unit.¹³³

Reactions Involving Aluminum Chloride as Catalyst

It was considered possible that the formation of small amounts of di- and tetraphenyldisilane from the reaction of hexaphenyldisilane with lithium aluminum hydride in tetrahydrofuran occurred by a redistribution reaction catalyzed by traces of aluminum chloride. However, this does not appear to be likely, since hexaphenyldisilane and Compound (B) were recovered in high yields after refluxing with aluminum chloride in tetrahydrofuran. When hexaphenyldisilane was similarly treated in benzene, only 66% was recovered, while just 14.7% of Compound (B) was found to be unreacted after stirring with aluminum chloride in nitrobenzene. Aluminum chloride has also been reported not to effect disproportionation of phenylsilane when refluxed in diethyl ether, whereas the reaction occurs readily in benzene.¹³⁴ Furthermore, no evidence of a reaction was observed between benzoyl chloride or benzyl chloride and benzene upon treatment with aluminum chloride in tetrahydrofuran. The exact cause of this unreactivity in tetrahydrofuran was not investigated. It may be due to a strong complex between

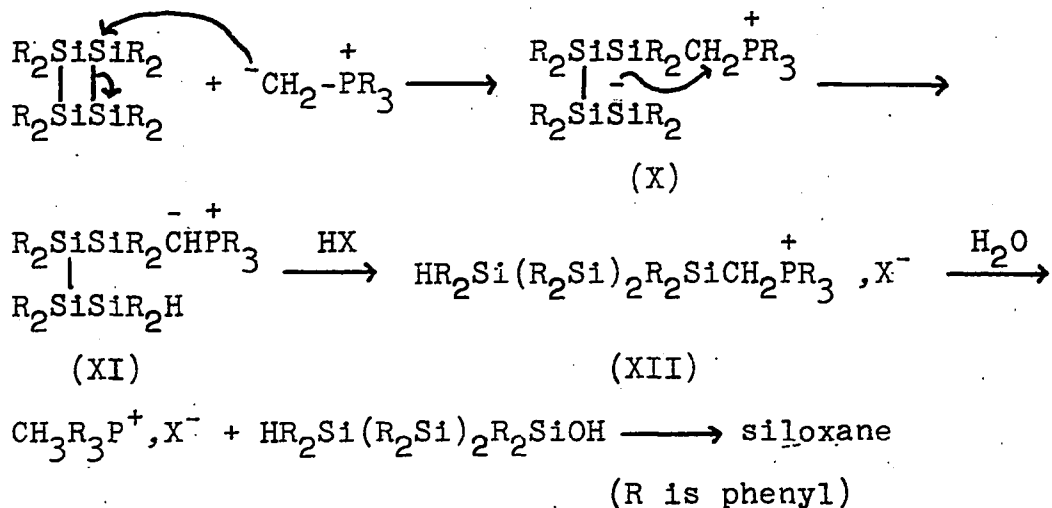
¹³³E. A. Zuech, "Cyclic Organosilicon and Related Compounds", unpublished Ph. D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa, 1960.

¹³⁴J. L. Speier and R. E. Zimmerman, J. Am. Chem. Soc., 77, 6395 (1955).

aluminum chloride and the solvent, or reaction with tetrahydrofuran itself.

Reactions Involving Wittig Reagents^{95,96}

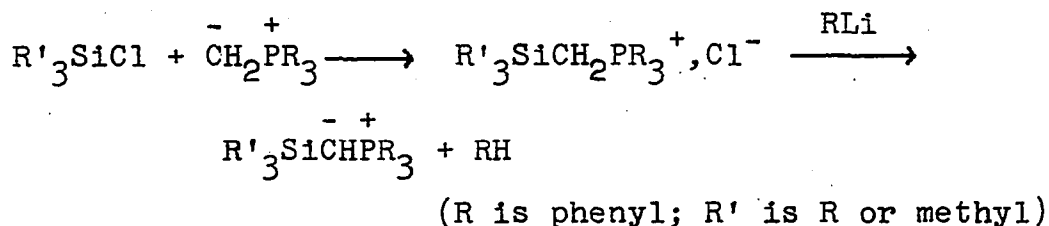
The fact that organometallic compounds cleave octaphenylcyclotetrasilane suggested that Wittig reagents might also react. The reaction with methylenetriphenylphosphorane was carried out in refluxing tetrahydrofuran and, subsequent to acid hydrolysis, products containing silicon-hydrogen, silanol and siloxane groups were obtained, along with recovered starting material and methyltriphenylphosphonium salts. These products indicated that the following reaction had occurred. An attempt to establish the presence of the



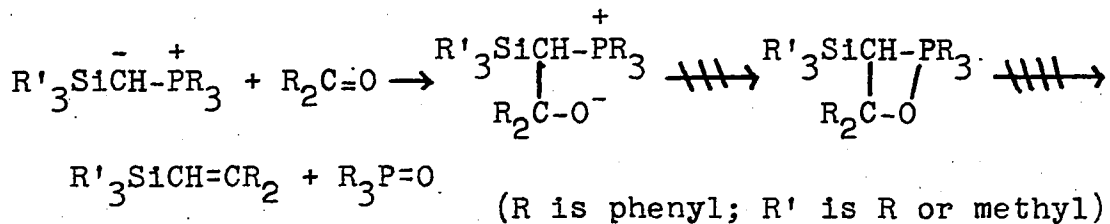
intermediate "ylide" (XI) by treatment with benzophenone did not afford any isolable diphenylvinyl-substituted product.

The recent preparation of a phosphonium salt of the type (XII) and its ready hydrolysis⁹⁷ supports the proposed

sequence of reactions, and suggested the possibility of synthesizing less complex organosilicon-substituted "ylides". and utilizing them in the formation of vinyl silicon compounds. Some preliminary investigations along this line were carried out. The difficulty experienced in isolating the phosphonium salt⁹⁷ led to the treatment of the salts, in situ, with phenyllithium. The reaction scheme is shown in the following equation. Color Tests I for phenyllithium



were negative or very weakly positive, showing that a reaction had occurred, presumably as shown in the preceding equation. However, treatment of the resulting mixtures with benzophenone in refluxing tetrahydrofuran did not lead to isolable amounts of diphenylvinyl-substituted organosilicon compounds, as would have resulted had the reaction taken the expected course illustrated in the following equation. Therefore, indications are that this type of



reaction does not provide a convenient synthetic approach to vinyl-substituted organosilicon compounds, at least under the conditions employed. The exact nature of the reactions is not clear, but some aspects will be discussed in the following paragraphs.

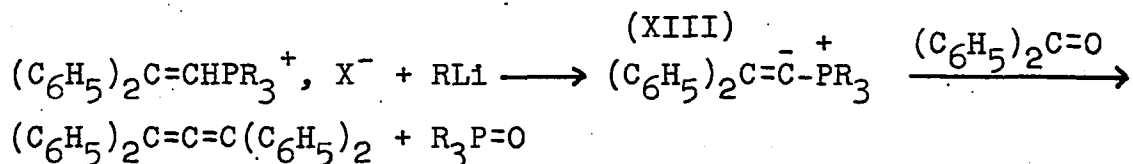
The previously unreported reaction between chlorotriphenylsilane and methylenetriphenylphosphorane produced a heavy, ether-insoluble precipitate, presumably the phosphonium salt. Treatment of this with phenyllithium caused the mixture to turn a dark brown. A Color Test I⁷⁵ for phenyllithium was negative after allowing the mixture to stir for two hours at room temperature. Benzophenone was added, the ether displaced by tetrahydrofuran and the resulting mixture refluxed. Subsequent to hydrolysis, solids formed which on work-up yielded methyltriphenylphosphonium salt and hexaphenyldisiloxane, evidently resulting from hydrolysis of the intermediate "ylide". From the ether soluble material, there was isolated more hexaphenyldisiloxane and triphenylsilanol, accounting for the majority of chlorotriphenylsilane used. Only traces of tetraphenylsilane were obtained, showing that attack at silicon in the phosphonium salt by phenyllithium did not occur to any appreciable extent. The fact that phenyllithium did react with the salt indicated that an "ylide" was formed. No (2,2-diphenylvinyl)triphenylsilane was isolated, perhaps due to the fact that the proposed "ylide" was unable to

react with benzophenone under the conditions employed. There was also isolated from the ether soluble fractions, a material melting at 123-124°, which was identified as a 1:1 mole complex between triphenylsilanol and triphenylphosphine oxide. The method of formation of triphenylphosphine oxide is not clear. Some oils were also obtained, the infrared spectrum of which indicated them to be primarily recovered benzophenone. Similar results were obtained when the reaction was carried out in xylene instead of tetrahydrofuran. An attempt to effect a reaction with Michler's ketone was unsuccessful. From this reaction, no triphenylphosphine oxide was isolated, and the ketone was recovered in high yield.

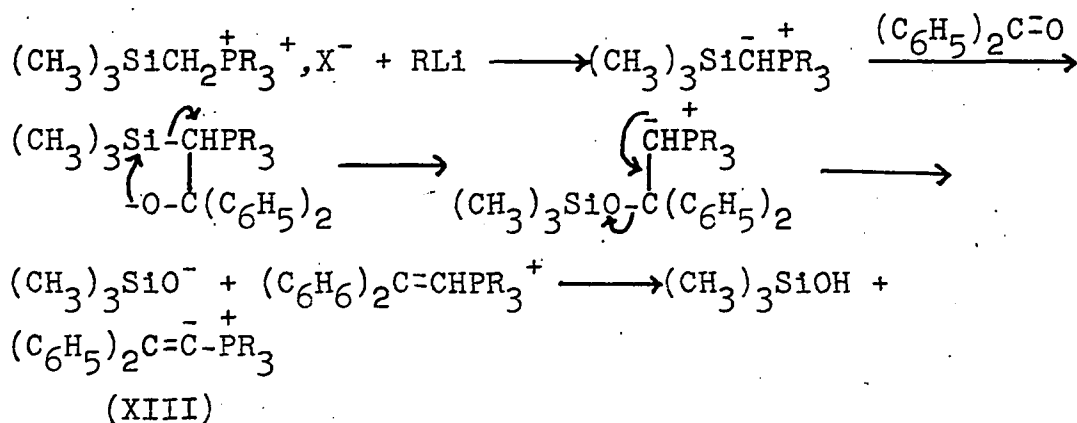
A similar sequence of reactions was carried out with chlorotrimethylsilane. From one experiment there was some material obtained which was apparently impure diphenylethylene containing a small amount of (2,2-diphenylvinyl)-trimethylsilane, as indicated by analysis, but this was not confirmed. A lesser amount of this material was obtained when the intermediate salt was reacted with phenyllithium under more vigorous conditions before addition of benzophenone. Some higher boiling products were also obtained, but were not investigated further.

From both of these runs, there was isolated a rather unexpected product, tetraphenylallene. The yield was around 20% in the first case and from the reaction using the

variation described in the preceding paragraph, the crude yield was 35%. This compound would be the expected product from the treatment of benzophenone with a "diphenylvinyl-ide", a reaction which was established in a separate experiment, as illustrated in the following equation. A mechanism



for the formation of the intermediate "ylide", (XIII) from the reaction involving chlorotrimethylsilane is shown in the following scheme.

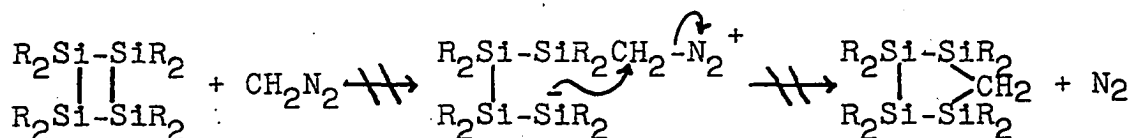


Thus it appears that under conditions wherein an alpha-silyl-substituted "ylide" does react with ketones, side reactions can occur to an appreciable extent. It appears that the solvent has an effect on the reaction, as no tetraphenylallene was isolated when the ether was displaced by xylene instead of tetrahydrofuran. As was the

case involving chlorotriphenylsilane, no products were obtained from the reaction with Michler's ketone in tetrahydrofuran. The ketone was recovered in good yield and there was no triphenylphosphine oxide isolated.

Attempted Reaction of Octaphenylcyclotetrasilane
with Diazomethane

A reaction between octaphenylcyclotetrasilane and diazomethane was considered as a means of interjecting a methylene unit between the silicon-silicon bonds to form a five-membered ring, as illustrated in the following equation.



However, no reaction was observed under the necessarily mild conditions employed. Octaphenylcyclotetrasilane was recovered in good yields.

SUGGESTIONS FOR FURTHER RESEARCH

Before the chemistry of organosilylaluminum compounds can be investigated, methods for their synthesis must be devised. Although the reaction between three equivalents of triphenylsilyllithium and aluminum chloride did not lead to appreciable amounts of a silylaluminum compound, experiments using one and two mole ratios should be investigated. Also, it is possible that the use of organoaluminum chlorides might prove fruitful. For example, reaction with diphenylaluminum chloride might afford diphenyl(triphenylsilyl)aluminum, as illustrated in the following equation. A

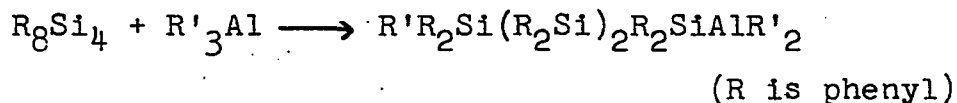
$$(\text{C}_6\text{H}_5)_3\text{SiLi} + (\text{C}_6\text{H}_5)_2\text{AlCl} \longrightarrow (\text{C}_6\text{H}_5)_3\text{SiAl}(\text{C}_6\text{H}_5)_2 + \text{LiCl}$$

similar reaction with triphenylaluminum may give lithium triphenyl(triphenylsilyl)aluminate. However, the recently reported reaction between triphenylsilyllithium and triphenylboron¹³⁵ to give the analogous complex leads one to suspect that this reaction has been or will shortly be investigated in other laboratories.

The reaction of octaphenylcyclotetrasilane with organolithium reagents leads to intermediate silyllithium compounds.^{89,90,93} The reactivity of this cyclic compound suggests the cleavage by organoaluminum reagents as a means

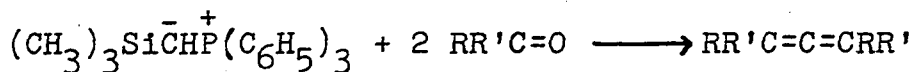
¹³⁵D. Seyferth, G. Raab, and S. O. Grim, J. Org. Chem., 26, 3034 (1961).

of forming silylaluminum derivatives, as illustrated in the following equation. However, this reaction may lead to

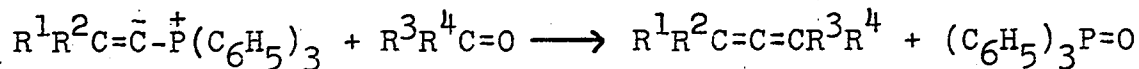


multiple cleavages and catenations giving a complex mixture of products. These side reactions may be decreased by the use of solvents other than tetrahydrofuran.

Although the synthesis of vinyl-substituted organosilicon compounds by the use of the Wittig reaction does not appear practicable, the results obtained suggest synthetic routes to allenes. Symmetrically substituted allenes could result from the corresponding carbonyl compounds using the trimethylsilyl-substituted "ylide", as shown in the following reaction scheme. Perhaps the use of n-butyllithium as the



metalating agent would prove more effective than phenyllithium. Synthesis of allenes with any degree of substitution should be feasible from vinyl-substituted "ylides" and carbonyl compounds, as shown in the following sequence of reactions. The potentiality of this method was demon-



strated by the synthesis of tetraphenylallene. However, before this technique could be used to advantage, a convenient synthetic approach to vinyl-phosphonium salts would have to be developed.

SUMMARY

A review of reductive cleavages of organosilicon compounds has been presented, with emphasis on reactions which involve fission of silicon-silicon and carbon-silicon bonds. In addition, a brief outline of the chemistry of octaphenylcyclotetrasilane has been included.

Octaphenylcyclotetrasilane was treated with a variety of reducing agents; of those tried, two systems were found which showed promise. They were hydrogenolysis over "copper chromite" at relatively high temperatures and hydrogen pressures, and cleavage by lithium aluminum hydride in tetrahydrofuran. These reactions were studied with less complex organosilicon compounds containing the disilane linkage.

The hydrogenolysis of silicon-silicon bonds over "copper chromite" to give the corresponding organosilicon hydrides was found to be a general reaction for phenyl-substituted compounds, but no reaction was observed with hexaethyldisilane upon similar treatment. The reaction was not catalyzed by palladium on charcoal, and only to a slight extent by Raney nickel. Attempts to hydrogenate the aromatic nuclei in phenyl-substituted organodisilanes over Raney nickel were unsuccessful.

The cleavage of the disilane linkage by lithium aluminum hydride in tetrahydrofuran was also shown to be specific for organosilanes containing phenyl substituents. Evidence which

strongly supports the formation of intermediate organo-silylaluminum compounds has been presented.

A preliminary investigation indicated that the use of alpha-silyl-substituted "ylides" was not a practicable method for the synthesis of vinyl organosilicon compounds by means of the Wittig reaction. In one case involving benzophenone, tetraphenylallene was isolated. The formation of tetraphenylallene suggested that vinyl "ylides" may provide a useful synthetic approach to allenes. This type of reaction was realized by the preparation of tetraphenylallene from benzophenone and (2,2-diphenylvinylidene)triphenylphosphorane.

It has been demonstrated that the conversion of silicon-hydrogen bonds into the corresponding chlorides by reaction with mercuric chloride may be accomplished in solvents such as benzene, ether, and tetrahydrofuran.

Aluminum chloride was found not to catalyze Friedel-Crafts reactions or disproportionation reactions of organosilicon compounds in the presence of tetrahydrofuran.

The reaction between tetramethylenemagnesium bromide and hexachlorodisilane leads to the formation of five-membered rings. No products containing the disilacyclohexane structure were isolated.

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation for the suggestions, advice, constructive criticisms, and encouragement received from Dr. Henry Gilman during the course of this work.

Thanks are also due to past and present research associates for fruitful discussions and aid in the preparation of this manuscript.

Samples of lithium aluminum deuteride were obtained through the generosity of Dr. Charles W. Heitsch, who also gave of his time in discussions on experimental details.

The author is grateful to Dr. Roy King and to Mrs. Ikue Ogawa for nuclear magnetic resonance and infrared spectral determinations.

This research was supported in part by the United States Air Force, under contracts monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

Finally, without the sacrifices and patience of the author's wife, Joan, this dissertation would not have been possible.